ORGANIC CHEMISTRY

CONSTITUTIONAL, GEOMETRIC, AND STEREO- ISOMERISM

CHEMISTRY 165 // SPRING 2020

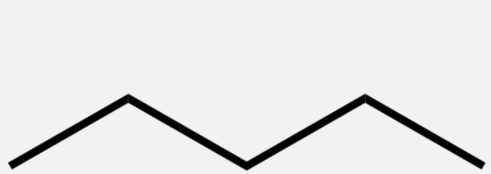
DR. MIOY T. HUYNH | 2020

Constitutional isomers

Consider the chemical formula for pentane: C_5H_{12}

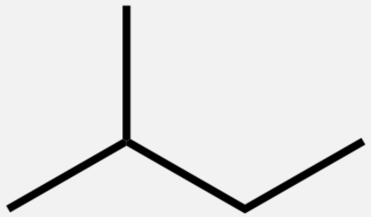
The simplest structure for such a chemical formula is a straight chain of 5 carbons (far left structure).

But we can also have other structures with the formula C_5H_{12}, which are drawn on the right.



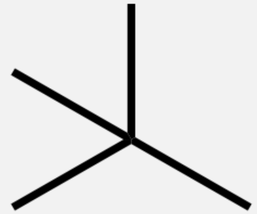
pentane

(C_5H_{12})



2-methylpentane

(C_5H_{12})



2,2-dimethylpropane

(C_5H_{12})

These are called **constitutional isomers** because they all have the same chemical formula (C_5H_{12}) but differ in the connectivity and bonding (i.e., the constitution) of the atoms.

PRACTICE PROBLEM 1

Draw and name any three constitutional isomers for C_4H_7F.

— answer —

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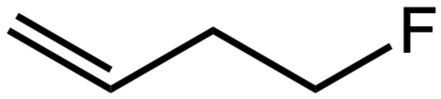
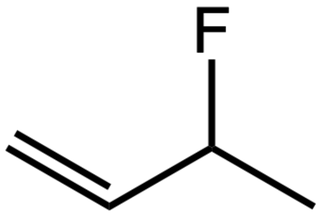
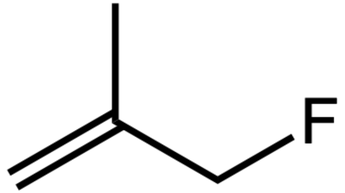


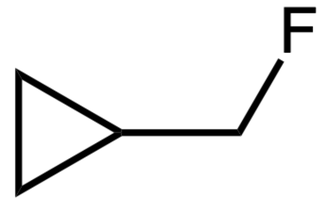
4-fluorobut-1-ene



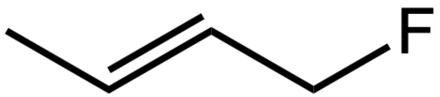
3-fluorobut-1-ene



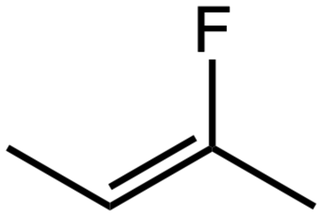
3-fluoro-2-methylprop-1-ene



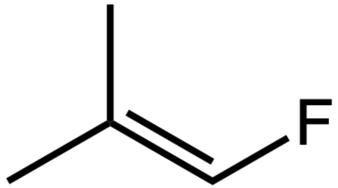
1-(fluoromethyl) cyclopropane



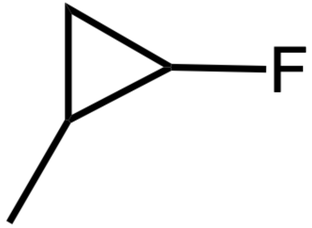
1-fluorobut-2-ene



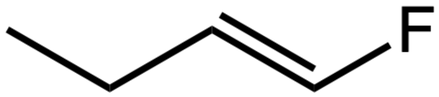
2-fluorobut-2-ene



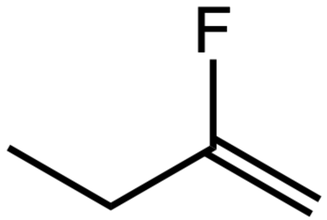
1-fluoro-2-methylprop-1-ene



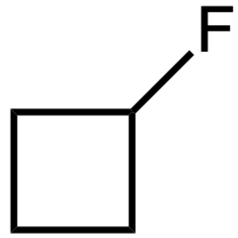
1-fluoro-2-methy lcyclopropane



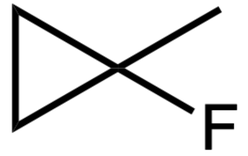
1-fluorobut-1-ene



2-fluorobut-1-ene



1-fluorocyclobutane



1-fluoro-1-methyl cyclopropane

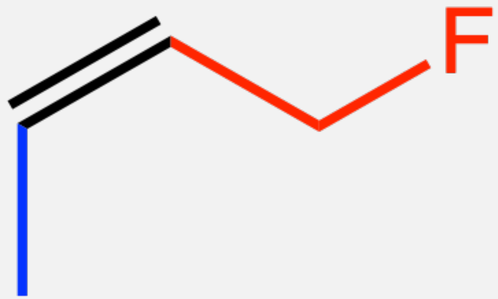
Geometric isomers (*cis-trans* isomers)

Let's take a closer look at 1-fluorobut-2-ene (C_4H_7F).

I can actually draw 1-fluorobut-2-ene in <u>two</u> *different* ways!

I have not changed the connectivity of the atoms, so these structures are <u>not constitutional isomers</u>.

The difference between the two structures is the relative orientations of the substituents coming off the double bond: a fluoromethyl- ($-CH_2F$) group and a methyl- ($-CH_3$) group.

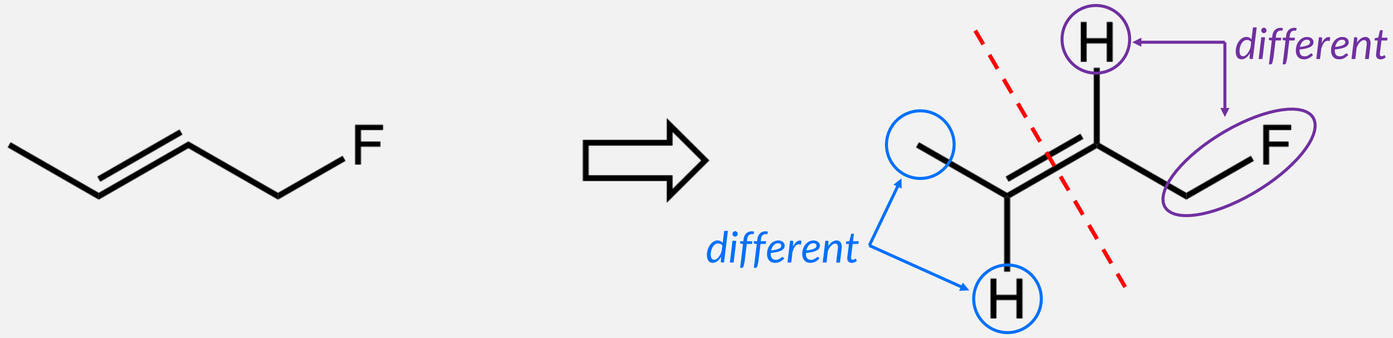


Notice that the methyl- group is on the opposite side of the fluoromethyl- group in the left structure, but they are on the same side of the double bond in the right structure.

These are called **<u>geometric isomers</u>** because they only differ in the geometry of the groups on the double bond.

How to tell if geometric isomers exist

Geometric (or *cis-trans*) isomerism can only exist if there are <u>two different groups</u> on each end of the double bond.



First, bisect the double bond (perpendicularly) down the middle (red dashed line).

Second, compare the groups on the left side: –H and $–CH_3$. These are two *different* groups.

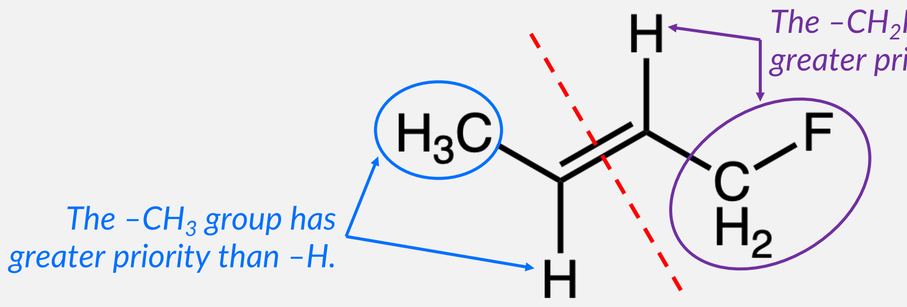
Third, compare the groups on the right side: –H and $–CH_2F$. These are two *different* groups.

Because each end of the double bond has two different groups attached to it,

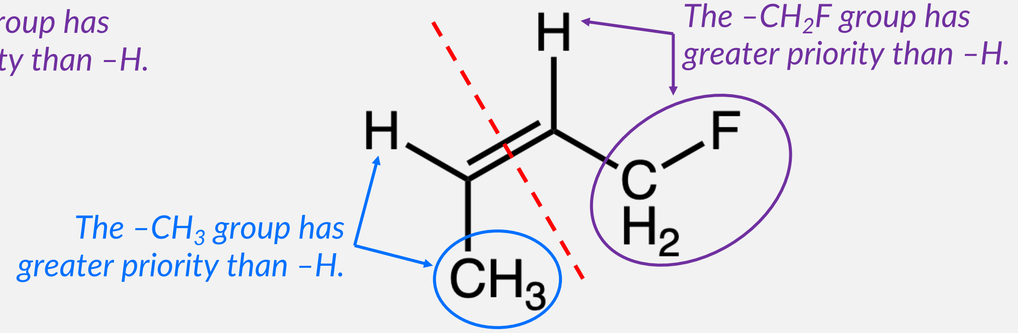
this molecule can have geometric (*cis-trans*) isomers!

Assigning *cis*- (*Z*-) and *trans*- (*E*-) isomers

Once we have established a molecule can have geometric isomers, we need to distinguish between the geometric isomers with some naming convention. Let's revisit the geometric isomers of 1-fluorobut-2-ene.



trans-1-fluorobut-2-ene
(*E*)-1-fluorobut-2-ene



cis-1-fluorobut-2-ene
(*Z*)-1-fluorobut-2-ene

First, bisect the double bond (perpendicularly) down the middle (red dashed line).

Second, we need to assign priorities to the groups on each side.

Priorities are assigned by atomic number, where heavier atoms (or groups) have greater priority.

If the two high priority groups (circled groups) are on the same side of the double bond → *cis*- or (*Z*-)

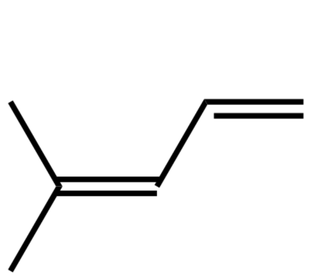
If the two high priority groups (circled groups) are on opposite sides of the double bond → *trans*- or (*E*-)

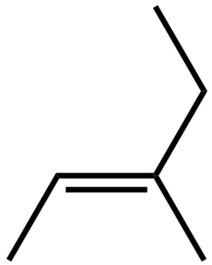
PRACTICE PROBLEM 2

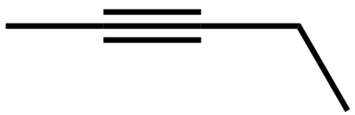
Determine if each of the following compounds can exhibit geometric isomerism.

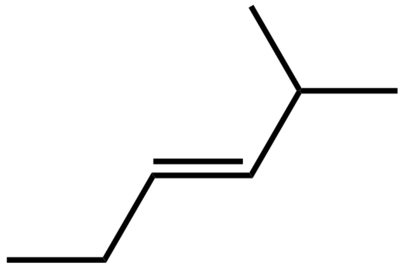
If it can, assign the relevant bond(s) as *cis*- (*Z*) or *trans*- (*E*).

— answer —









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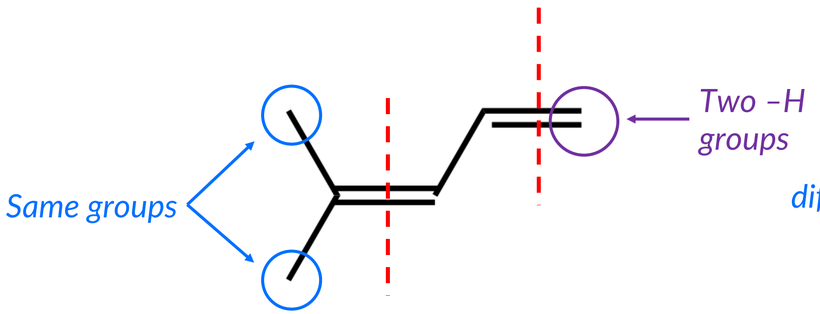
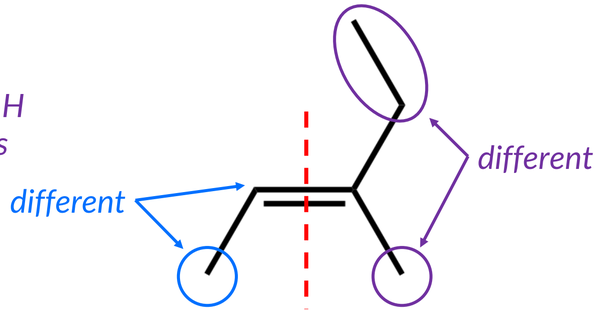
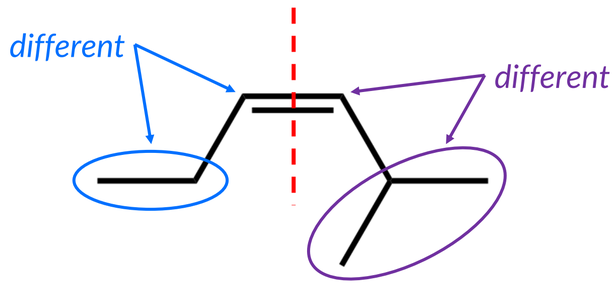
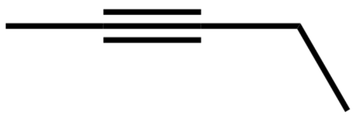


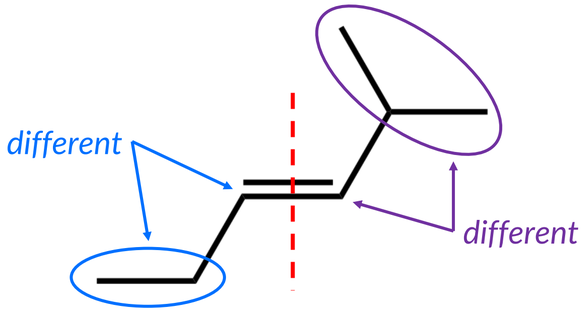




No geometric isomerism



No geometric isomerism
Alkyne bonds are linear.



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If it can, assign the relevant bond(s) as *cis*- (*Z*) or *trans*- (*E*).

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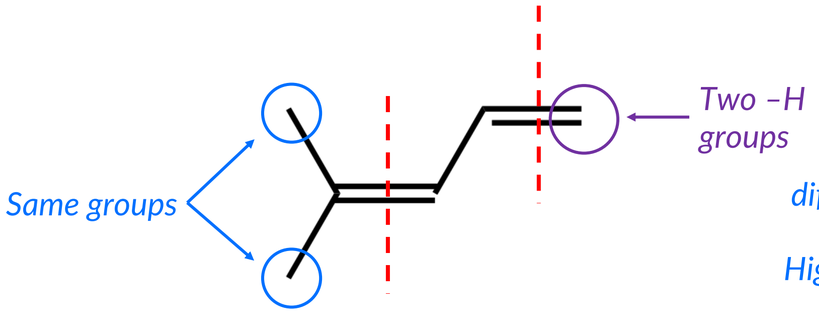
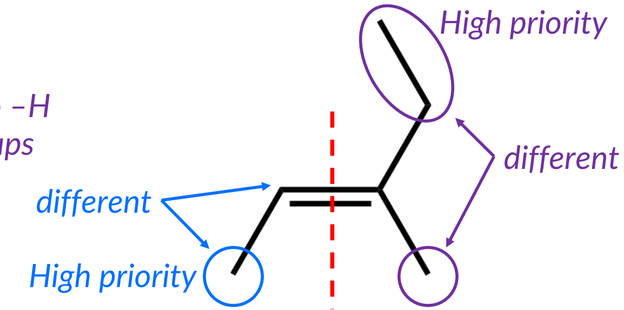
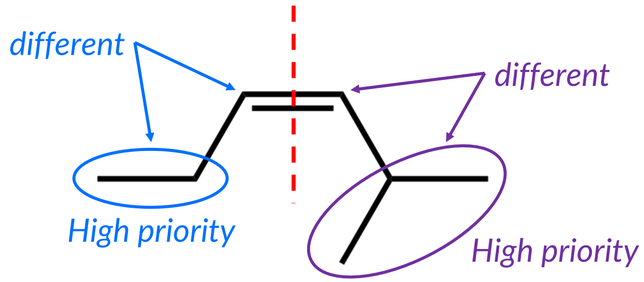


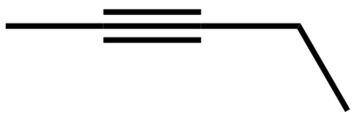
No geometric isomerism



trans-3-methylpent-2-ene
(E)-3-methylpent-2-ene



cis-2-methylhex-3-ene
(Z)-2-methylhex-3-ene



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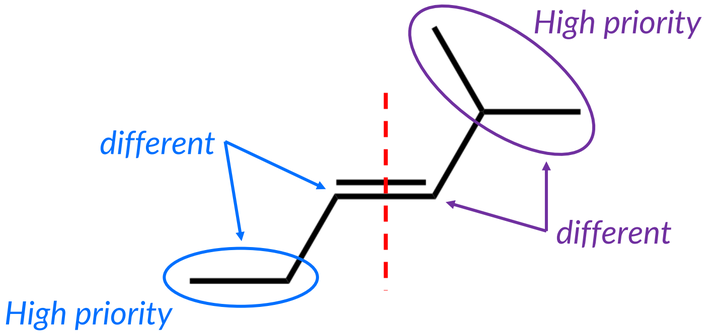


trans-2-methylhex-3-ene
(E)-2-methylhex-3-ene

Stereoisomers: chiral centers

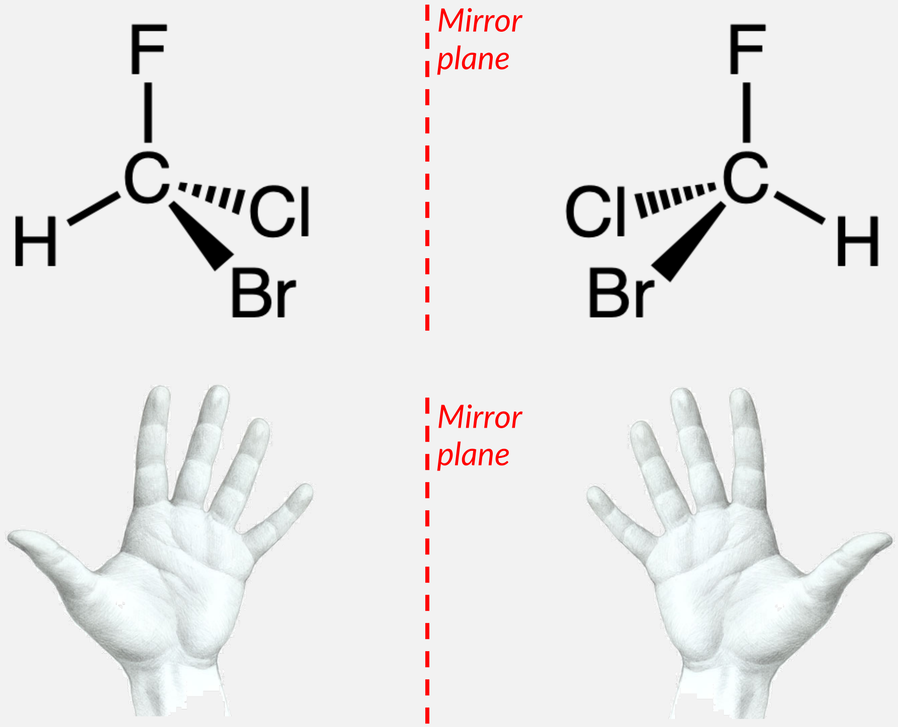
A **chiral carbon atom** is an sp^3-hybridized carbon atom bonded to 4 different groups.

The simplest chiral carbon atom to consider is **C**HBrFCl. The two stereoisomers for this molecule are drawn below. These are actually two different molecules! The two stereoisomers look similar; in fact, they are mirror images of each other, but no rotation of one isomer will ever give you the other identically.

Consider the similarities between the stereoisomers drawn and your hands.

Both images show that one is a mirror image of the other, but there are no operations (rotations, translations) that will ever make them identical.

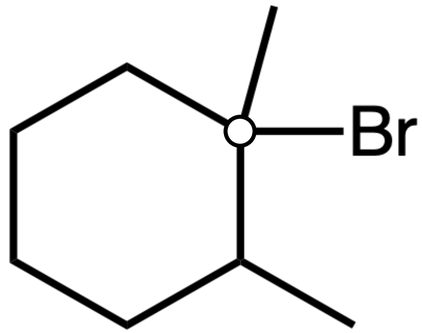
In other words, stereoisomers are non-superimposable mirror images.



Stereoisomers: dealing with rings

Let's take a look at 1-bromo-1,2-dimethylcyclohexane.

Q: Is carbon atom 1 (open circle) a chiral center?



First, look at the groups attached at C1:

- CH_3
- Br
- Rest of ring in clockwise (CW) direction
- Rest of ring in counterclockwise (CCW) direction

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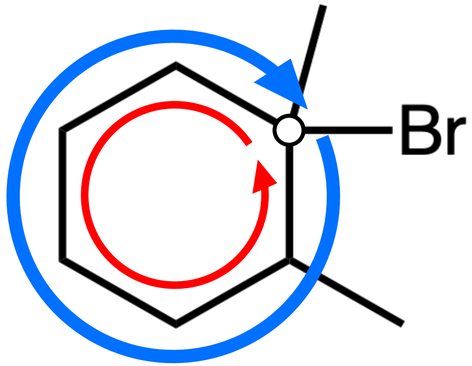

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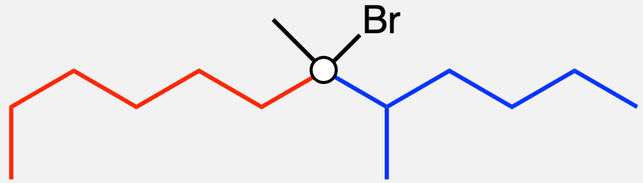
The $-CH_3$ and –Br groups are clearly different. But what about the other groups (i.e. the rest of the ring in the CW and CCW direction)? You can check this by "walking" along the ring in those directions to see that they are actually different groups.

I like to imagine breaking the ring into two chains: one for the CW and one for the CCW direction.



A: Carbon atom 1 is a chiral center!

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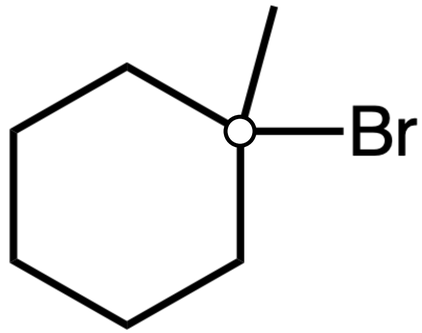

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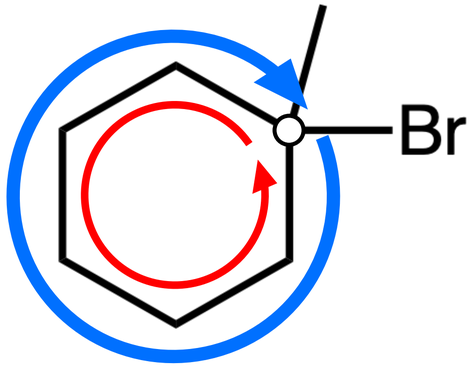

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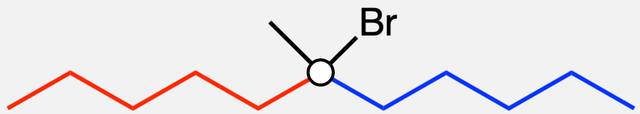
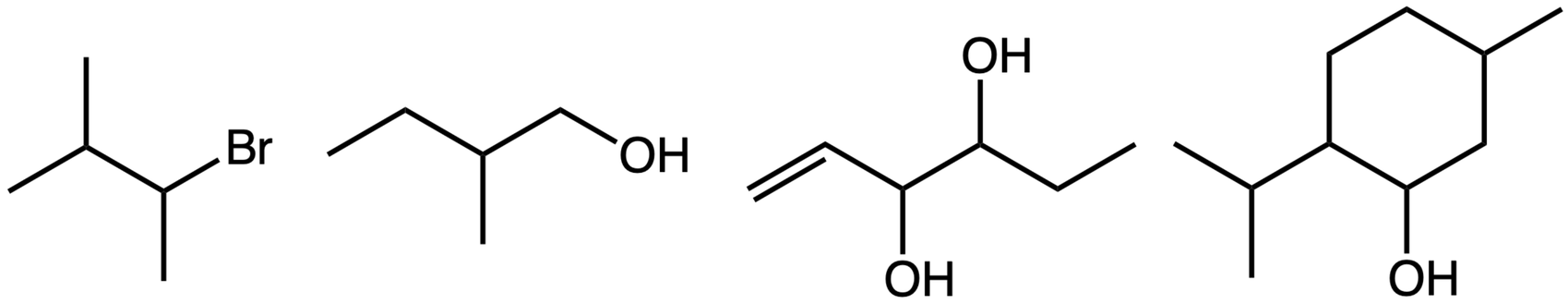


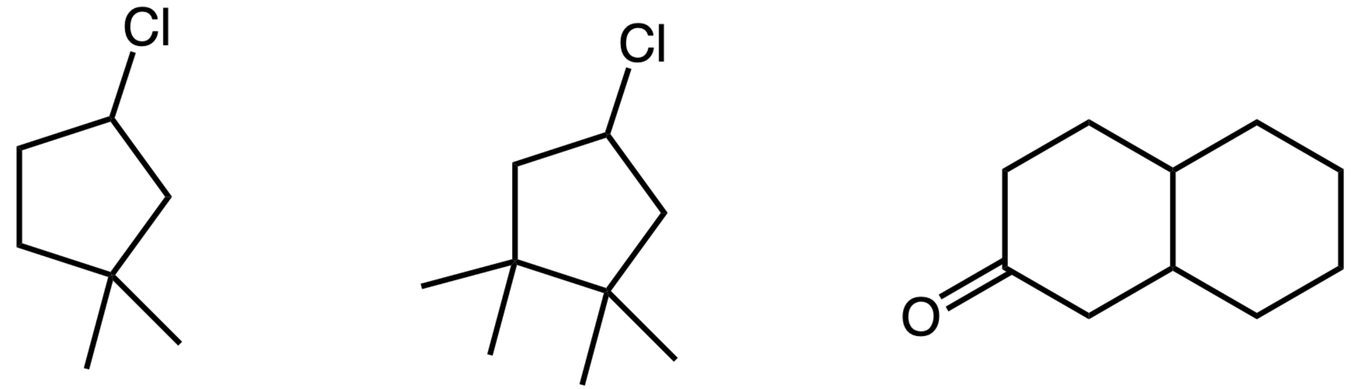
A: Carbon atom 1 is not a chiral center!

PRACTICE PROBLEM 3

For each of the following, identify any chiral center(s), if they exist.

— answer —





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