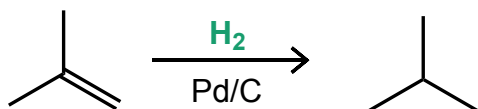


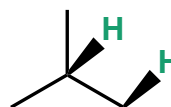
## Addition to Alkenes ( $\pi$ bonds)

As noted in the Additions Core Concepts, the mechanism of a reaction determines the selectivity observed in the product (Markovnikov vs. anti-Markovnikov regioselectivity or syn vs. anti stereospecificity of addition).

In some cases, primarily with linear (acyclic) alkenes, the selectivity is not apparent in the product. An example is given below:

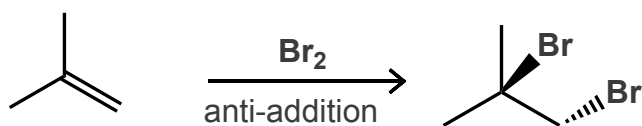


Some students may draw the product as:

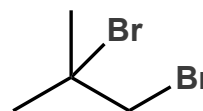


Although the structure above clearly shows a **syn addition**, this level of detail is not included in the line structure because 1) C—H bonds are not shown in line structures; 2) C—C single bonds can rotate freely, so the C—H bonds are not locked in place

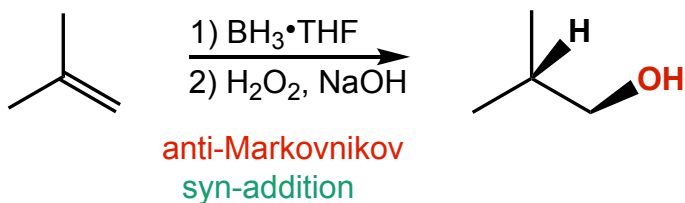
1. Correct the product structures shown below, and explain why the new line structure you draw still indicates the correct selectivity observed in these reactions.



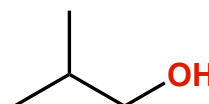
line structure



**Explanation:** Although the Br atoms are initially added anti to one another, free bond rotation around the new C-C bond and the absence of any stereocenters prevents the need to show dash/wedge bonds.

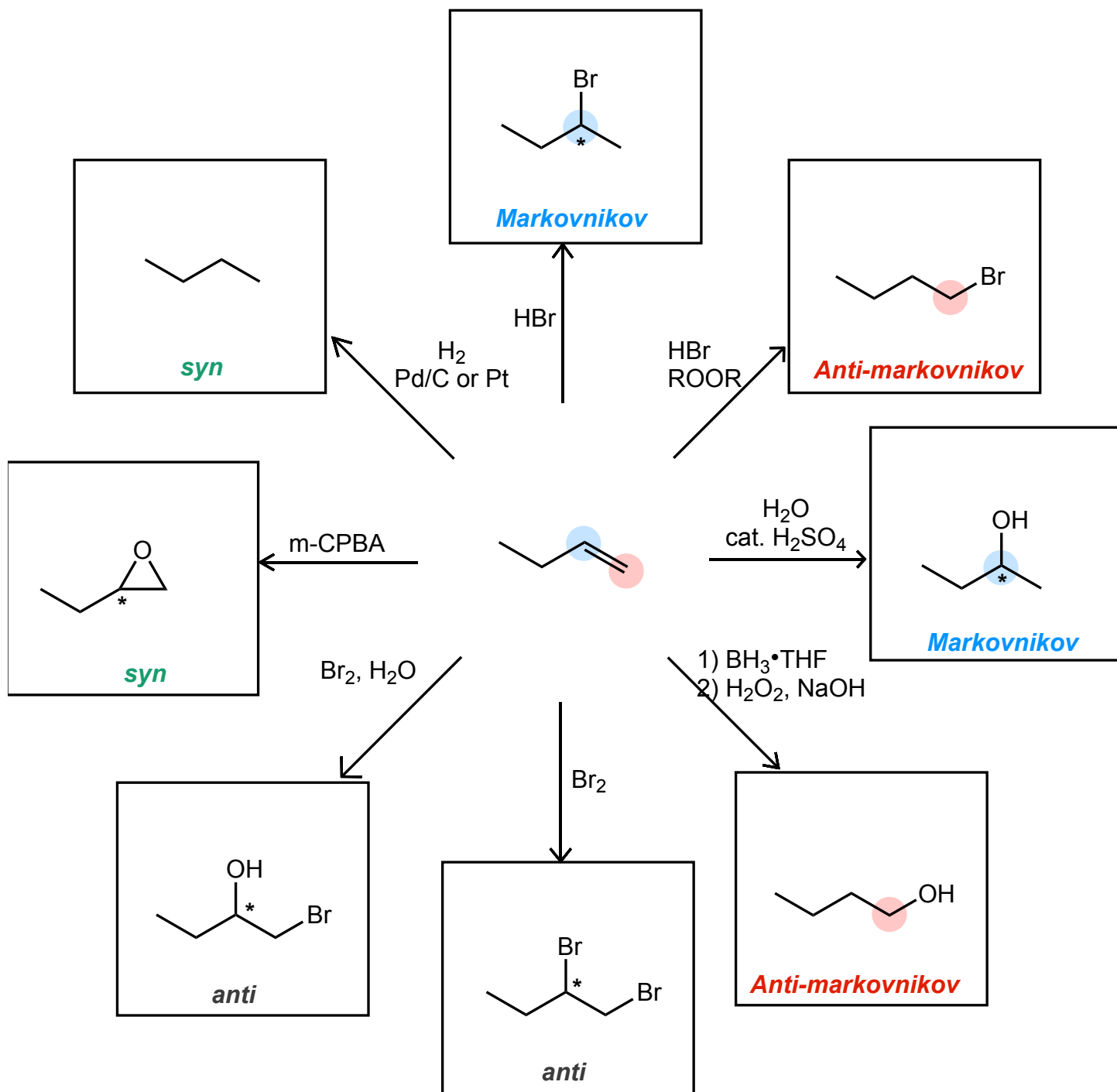


line structure

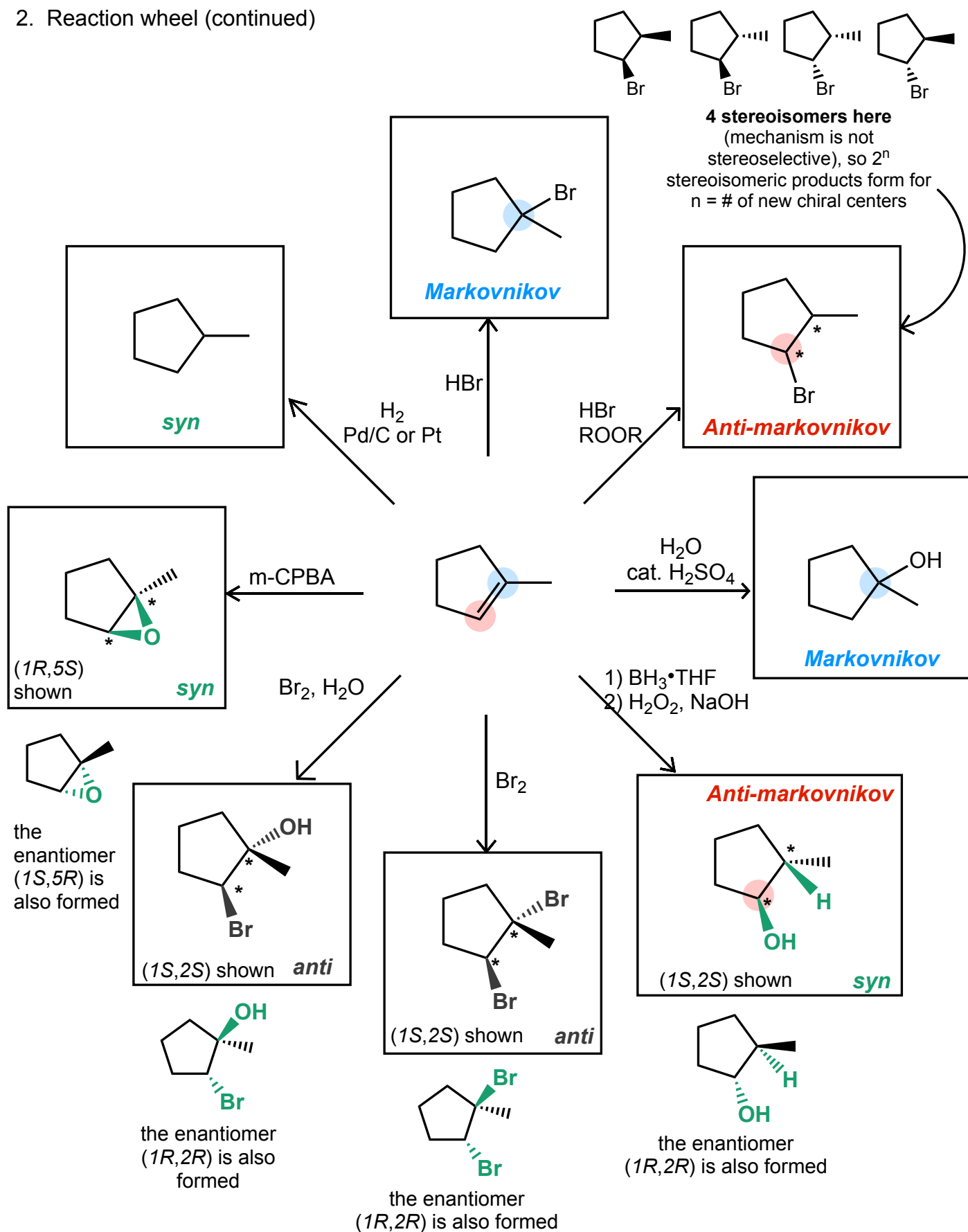


**Explanation:** No need to draw C-H bonds and although a syn-addition takes place in step 1, free bond rotation around the new C-C bond and the absence of any stereocenters prevents the need to show dash/wedge bonds.

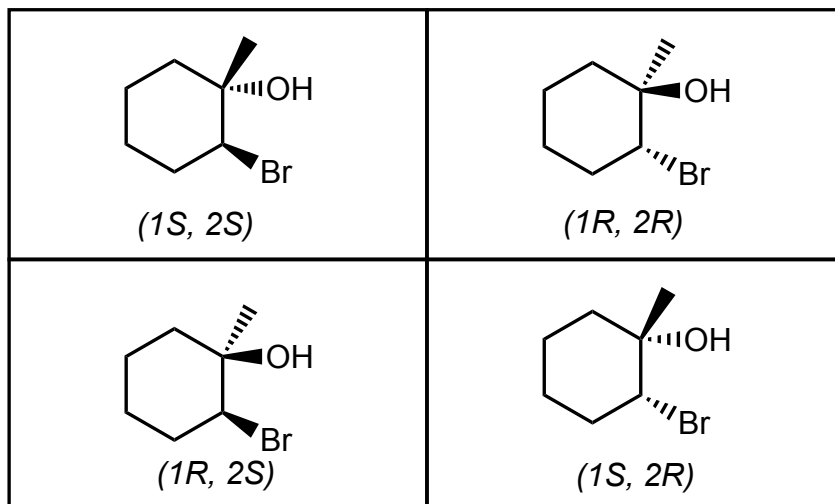
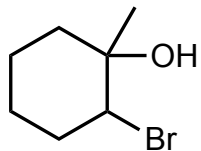
2. Reaction wheels are a great way to compartmentalize the multiple reactions that one specific functional group can undergo. What follows are two reaction wheels, one for an acyclic alkene, and one for a cyclic alkene. For these wheels, draw a line structure for the major organic product (using dash/wedge when necessary) and where appropriate, characterize the reactions using the terminology from the Additions Core Concepts (Markovnikov/anti-Mark.; syn/anti).



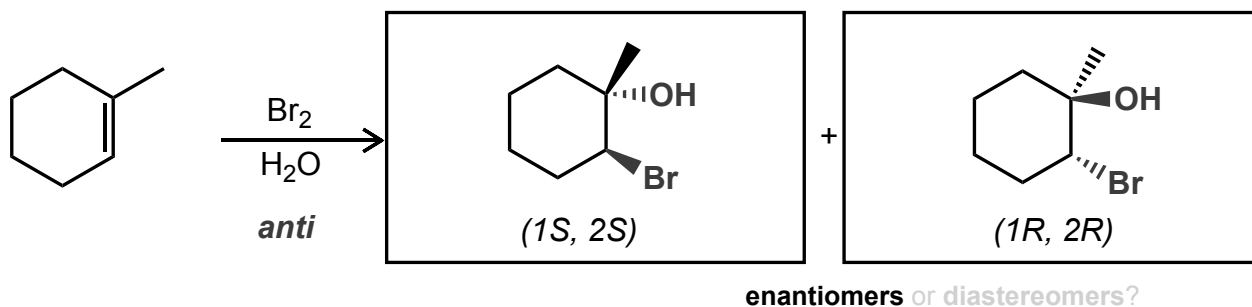
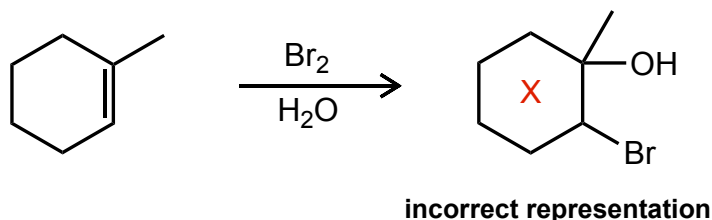
2. Reaction wheel (continued)



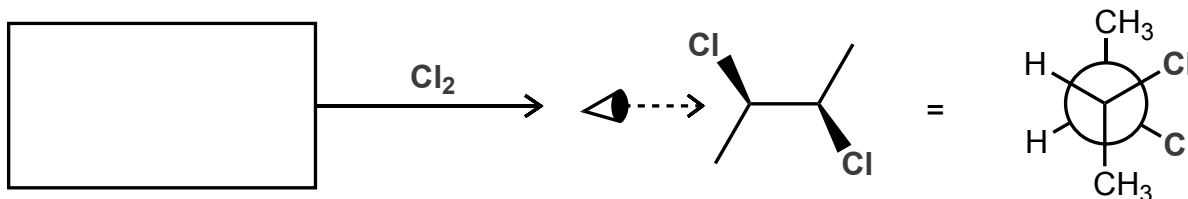
3. In the boxes provided, **draw the stereoisomers** that exist for the bromohydrin shown below.



4. A common mistake is to draw the product of the following reaction as shown below. From the stereoisomers you drew above, **draw the only two stereoisomers which can be formed from this reaction** in the boxes provided below. What is their relationship to each other (enantiomers or diastereomers)?



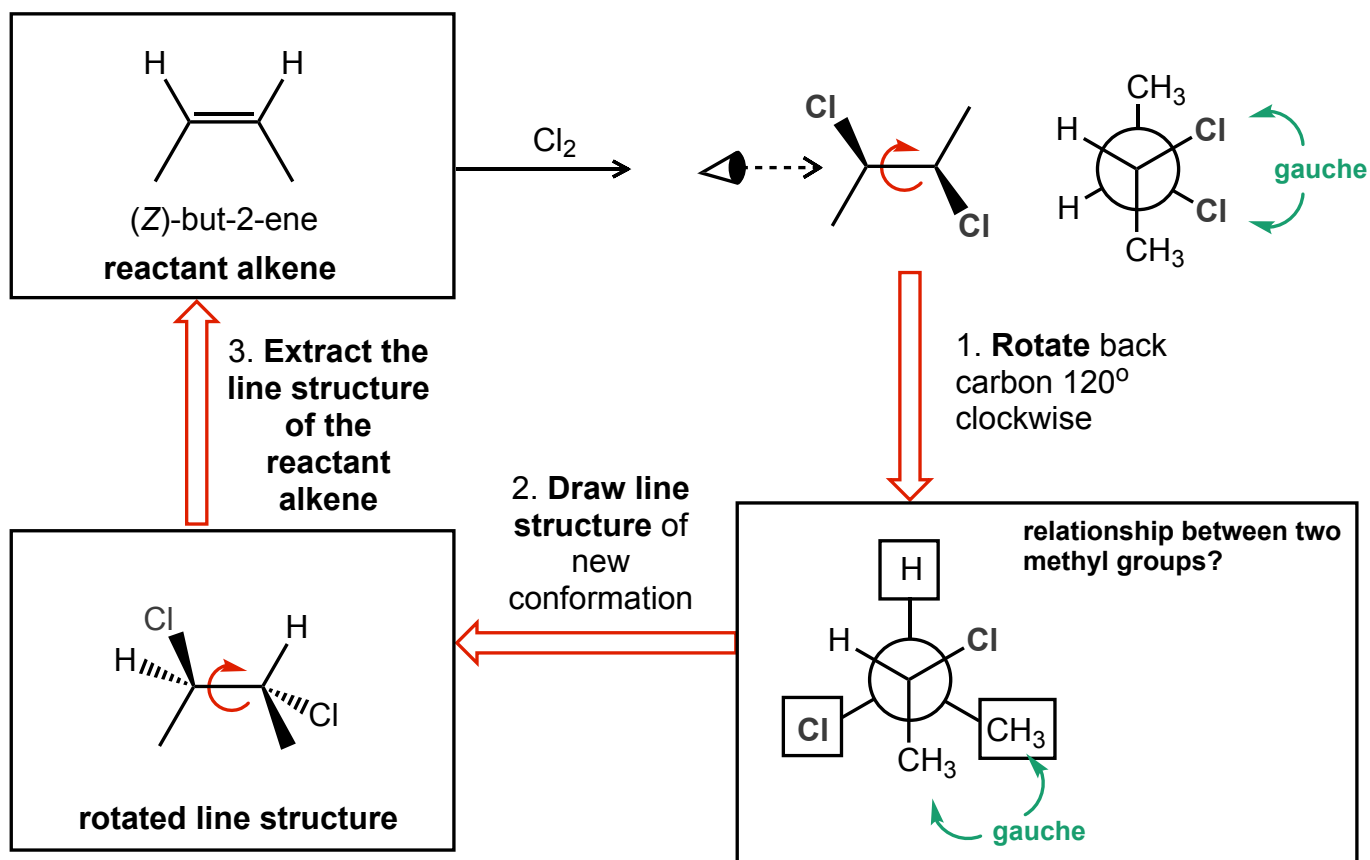
5. When determining the reactant used in an addition reaction, **bond rotation in the product must be considered**. As an example, consider the reaction shown below. Given the Newman projection shown on the right, how do you know that a bond rotation has occurred after the reaction took place?



**Explanation:** *Since the addition of  $\text{Cl}_2$  is an anti-addition reaction, the Cl atoms end up anti to one another immediately after the reaction is complete. In this case, the Cl atoms are gauche, therefore a bond rotation has occurred following the reaction.*

A. To answer this, 1) **rotate the Newman projection so that the Cl atoms are anti to one another**. Keeping in mind the stereochemistry shown, add in the missing groups on the back carbon after an appropriate bond rotation. Then 2) draw the rotated line structure of the product and 3) draw the reactant alkene in question.

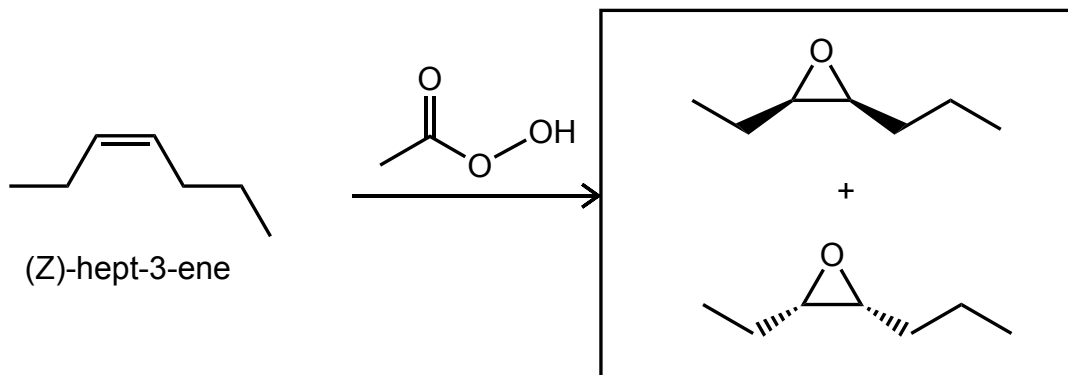
**Make note of the new relationship between the methyl groups** and with this information, **predict the structure of the reactant alkene**.



Once the C-C bond is rotated, a new Newman projection is generated on the bottom right. This shows that **when the Cl atoms are anti to each other, the methyl groups end up gauche to one another**. Redrawing this as a line structure shows that the methyl groups must have originally been positioned on the same side of the C=C bond, therefore the reacting alkene was the Z isomer. Had the methyl groups been antiperiplanar in the Newman projection on the bottom right, the alkene would have a trans relationship between the methyl groups.

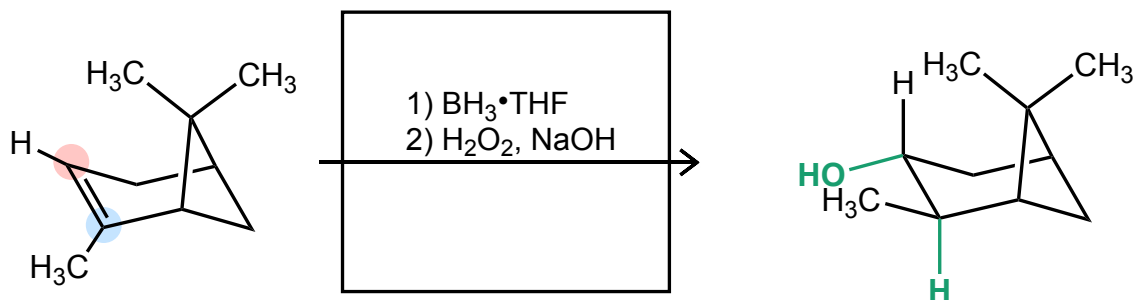
5. Provide the missing starting materials, reagents, or products of each reaction below.

A.



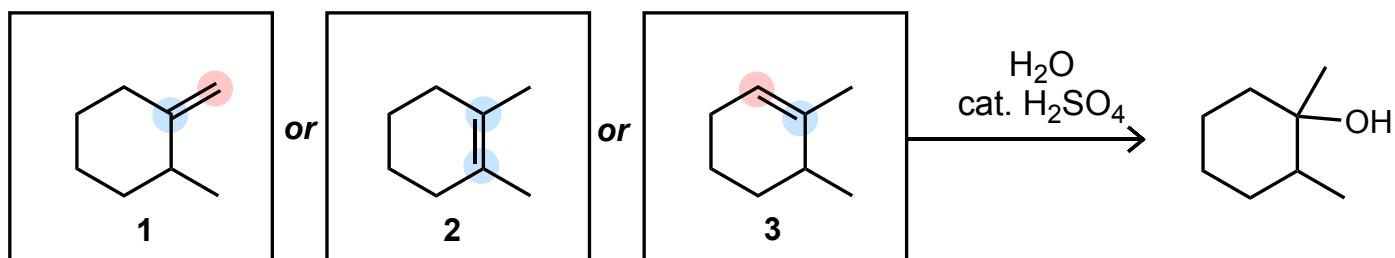
Since this reaction mechanism is concerted, the relationship of the ethyl groups on the alkene is retained in the product (cis on the C=C to cis on the epoxide)

B.



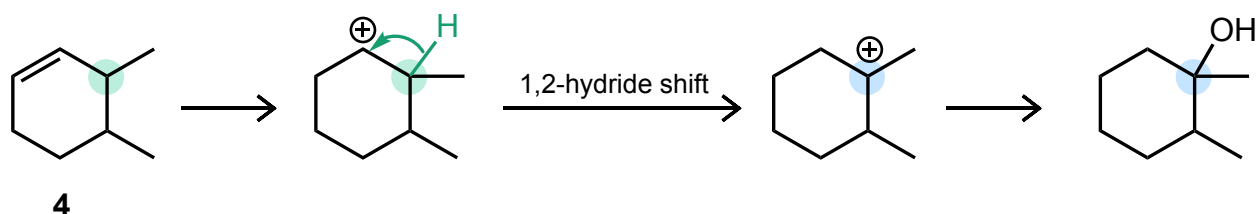
Overall, water has been added across the double bond, with the OH group being added to the least substituted C atom of the original C=C bond. To accomplish this **anti-Markovnikov syn**-addition requires a hydroboration reaction.

C. Three reactants are possible (without any carbocation shifts). Provide their structures.

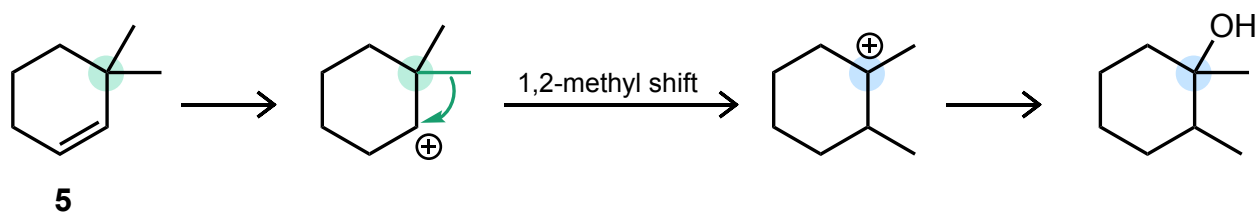


**1/2/3** - Each of these alkenes generates a 3° carbocation upon addition of a proton to the red C atom of the original C=C bond. Water attacks the carbocation (at the blue carbon) and then deprotonation generates the resulting alcohol.

Starting materials possible through carbocation shifts:



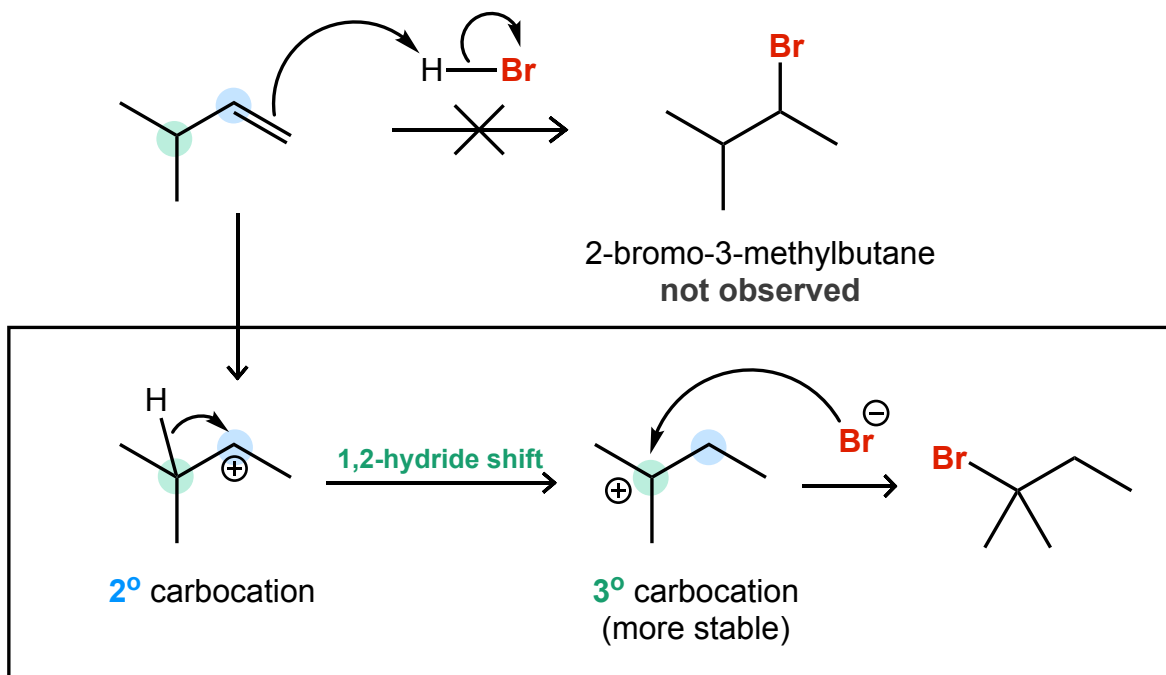
**4** - Addition of a proton to the leftmost carbon of the C=C bond generates a 2° carbocation which is adjacent to a 3° C atom (green carbon). A 1,2-hydride shift generates the 3° carbocation (now represented as the same blue carbon from reactants **1/2/3**) required to create the resulting alcohol.



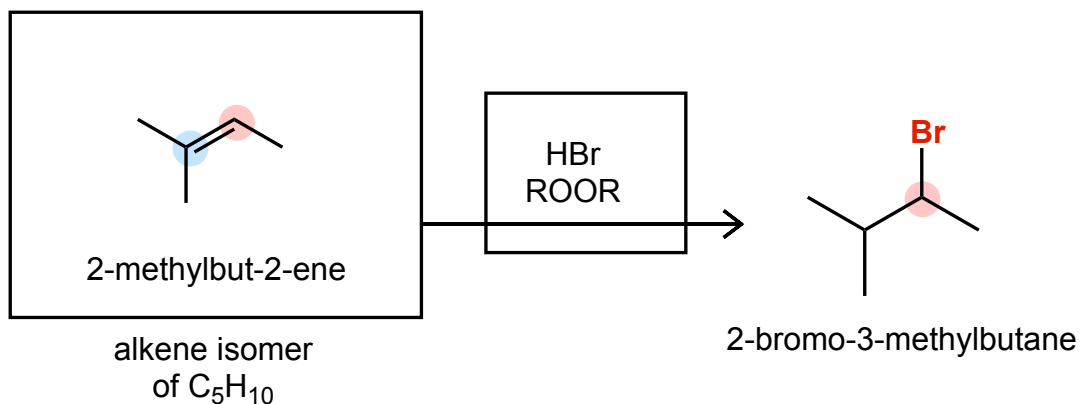
**5** - Addition of a proton to the bottom carbon of the C=C bond generates a 2° carbocation which is adjacent to a 4° C atom (green carbon). A 1,2-alkyl (methyl) shift generates the 3° carbocation (now shown as blue) required to create the resulting alcohol.

6. The addition of HX is an example of a stepwise mechanism that involves the formation of a carbocation.

A. By drawing the curved arrow mechanism, explain why 2-bromo-3-methylbutane is not formed as the major product. What product is formed?



B. Propose a reaction involving a constitutional isomer of the alkene above that would result in the formation of 2-bromo-3-methylbutane.



Starting from 2-methylbut-2-ene, the target product has Br at the **least** substituted carbon of the original C=C bond (blue C atom). This product can be generated using a reaction that undergoes an **anti-Markovnikov** addition reaction. For this reason, HBr in the presence of peroxides is an appropriate reagent to carry out this reaction.