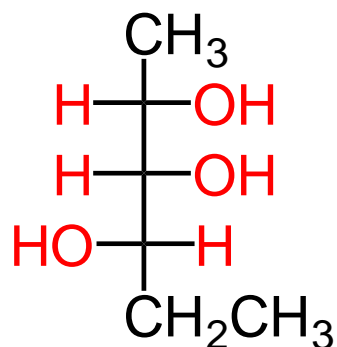
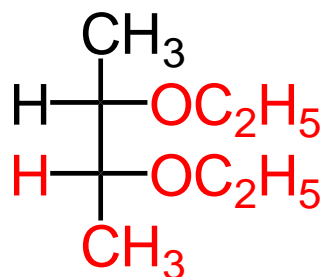


1.

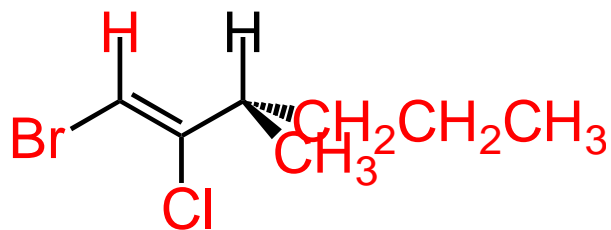
- a. Complete the following partial Fischer structure of (2S,3S,4S)-2,3,4-hexanetriol:



- b. Complete the following partial Fischer structure of meso-2,3-diethoxybutane:

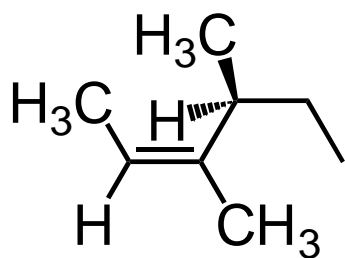


- c. Complete the following partial structure of (Z,3S)-1-bromo-2-chloro-3-methyl-1-hexene:



2. Name the following compounds by the IUPAC system. The name must indicate the stereochemistry of the compound.

a.



(Z,4S)-3,4-dimethyl-2-hexene

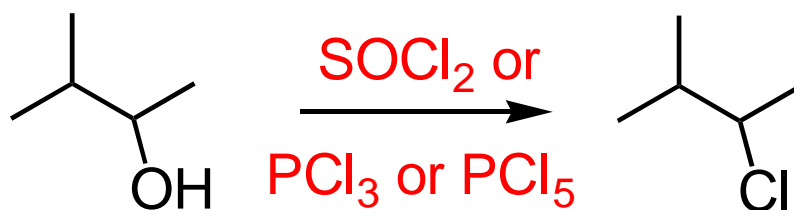
b.



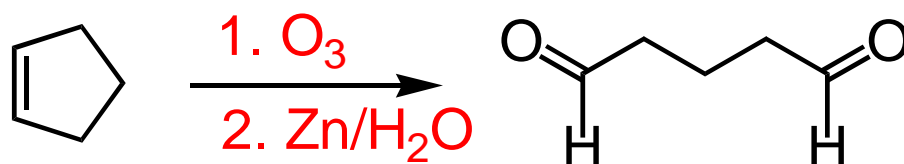
(1R,2S,3S)-2,3-dibromocyclohexanol

3. What reagents would you use to effect the following conversions?

a.



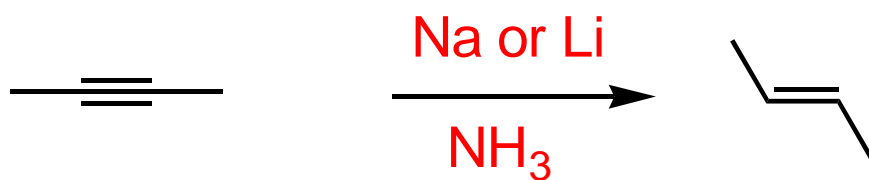
b.



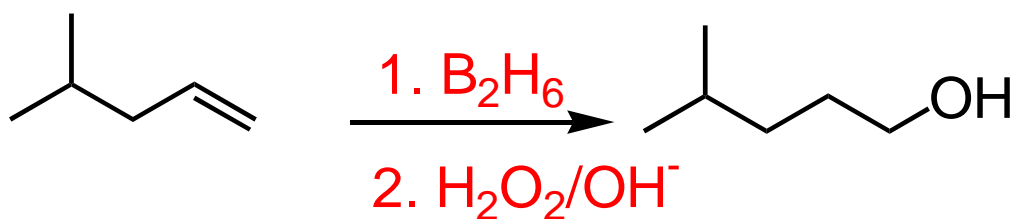
c.



d.

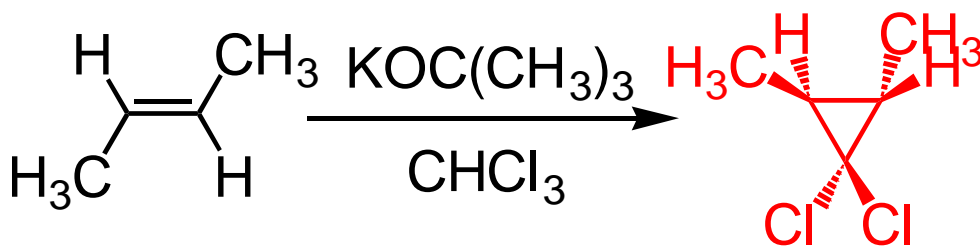


e.

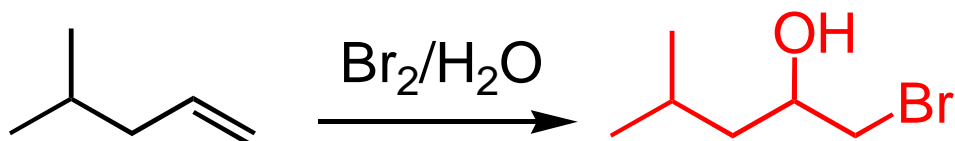


4. Give the structure(s) of the principle organic products of the following reactions. Where appropriate the structures must indicate the stereochemistry of the compound:

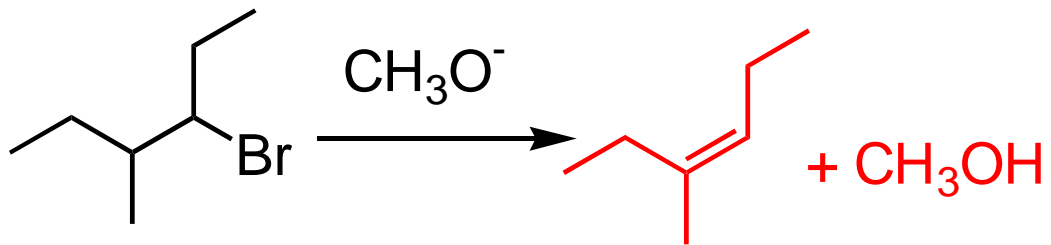
a.



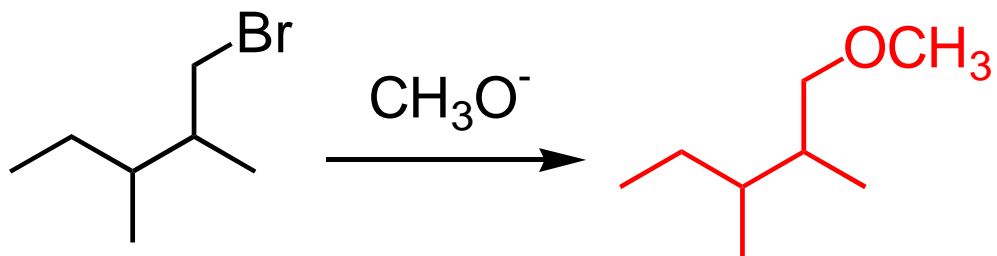
b.



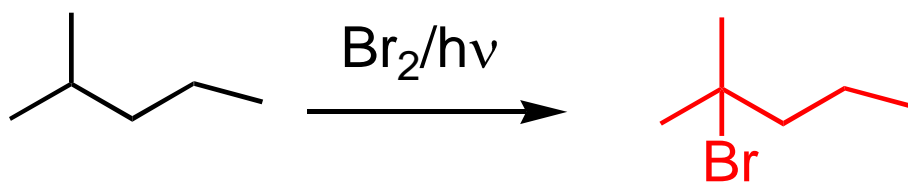
c.



d.

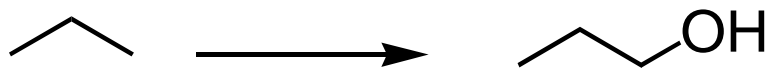


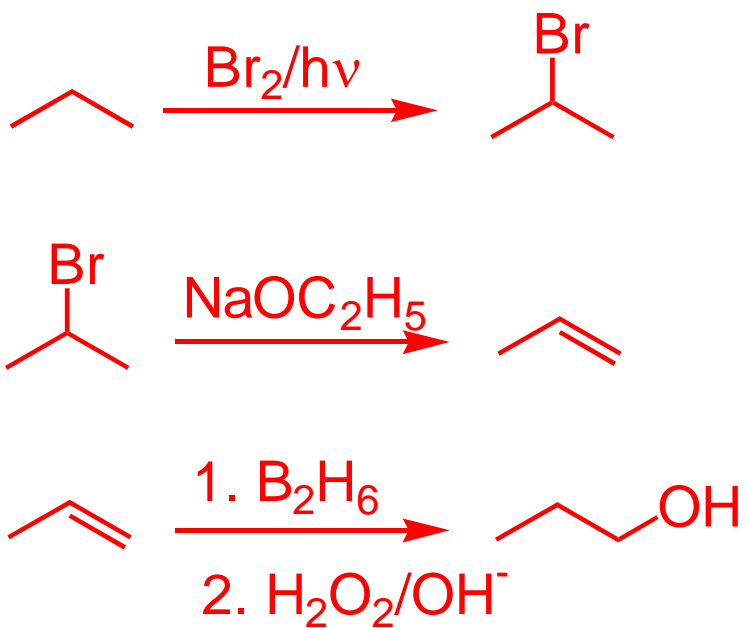
e.



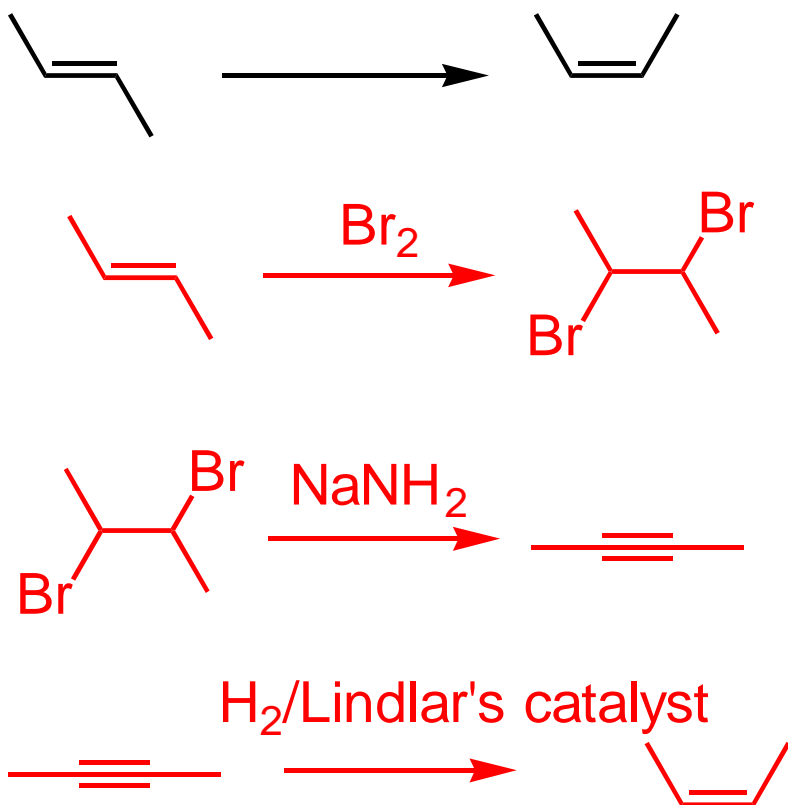
5. Provide a synthetic pathway for the following transformations. Begin your synthesis with the indicated starting material.

a.

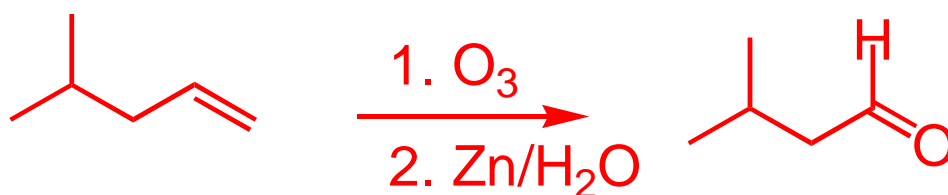
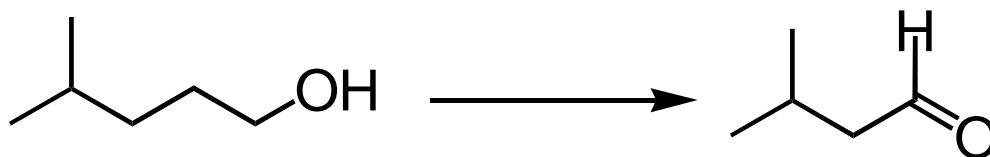




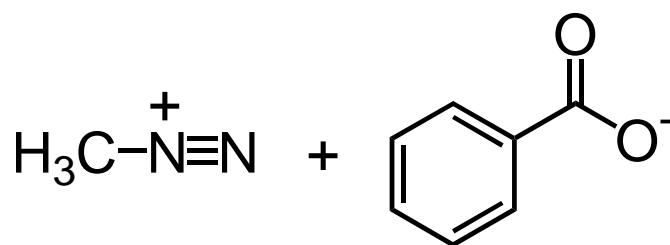
b.



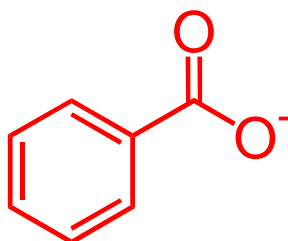
c.



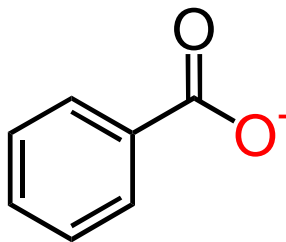
6. a. For the following reaction, identify the nucleophile, its nucleophilic atom, the electrophilic atom in the substrate molecule, and the leaving group. Write the organic product of the reaction.



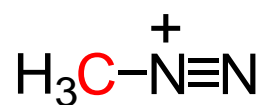
nucleophile =



nucleophilic atom =



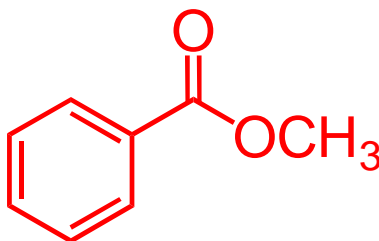
electrophilic atom =



leaving group =



organic product =



b. Select the member of each pair of compounds that will react faster by an $\text{S}_{\text{N}}2$ mechanism:

i. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{I}$ or $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$

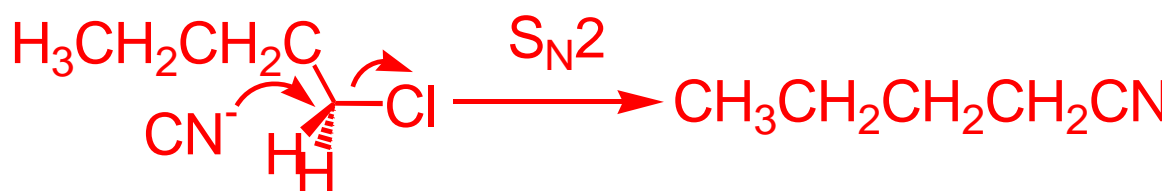


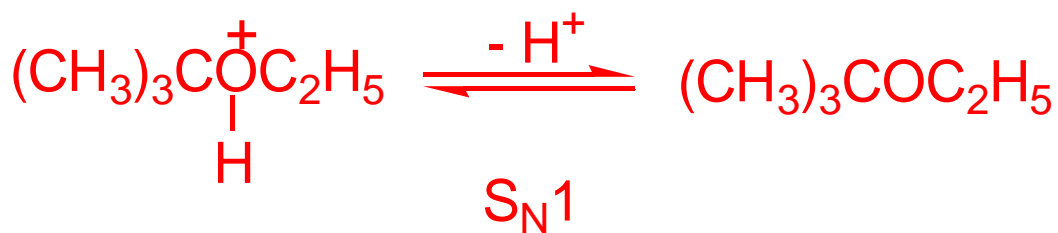
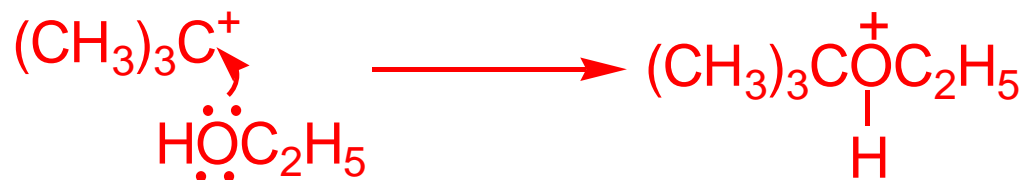
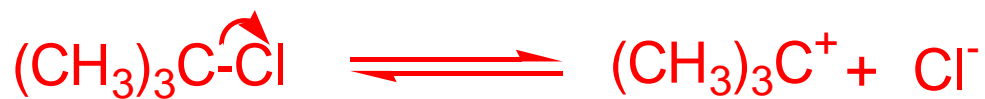
ii. $(\text{CH}_3)_2\text{CHCH}_2\text{Cl}$ or $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$



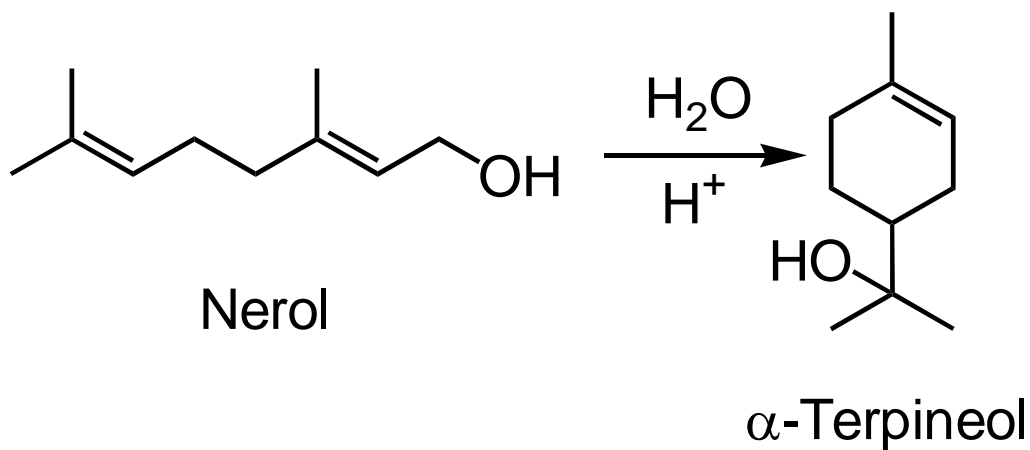
c. Which reagent in each pair would be the better nucleophile in a protic solvent?

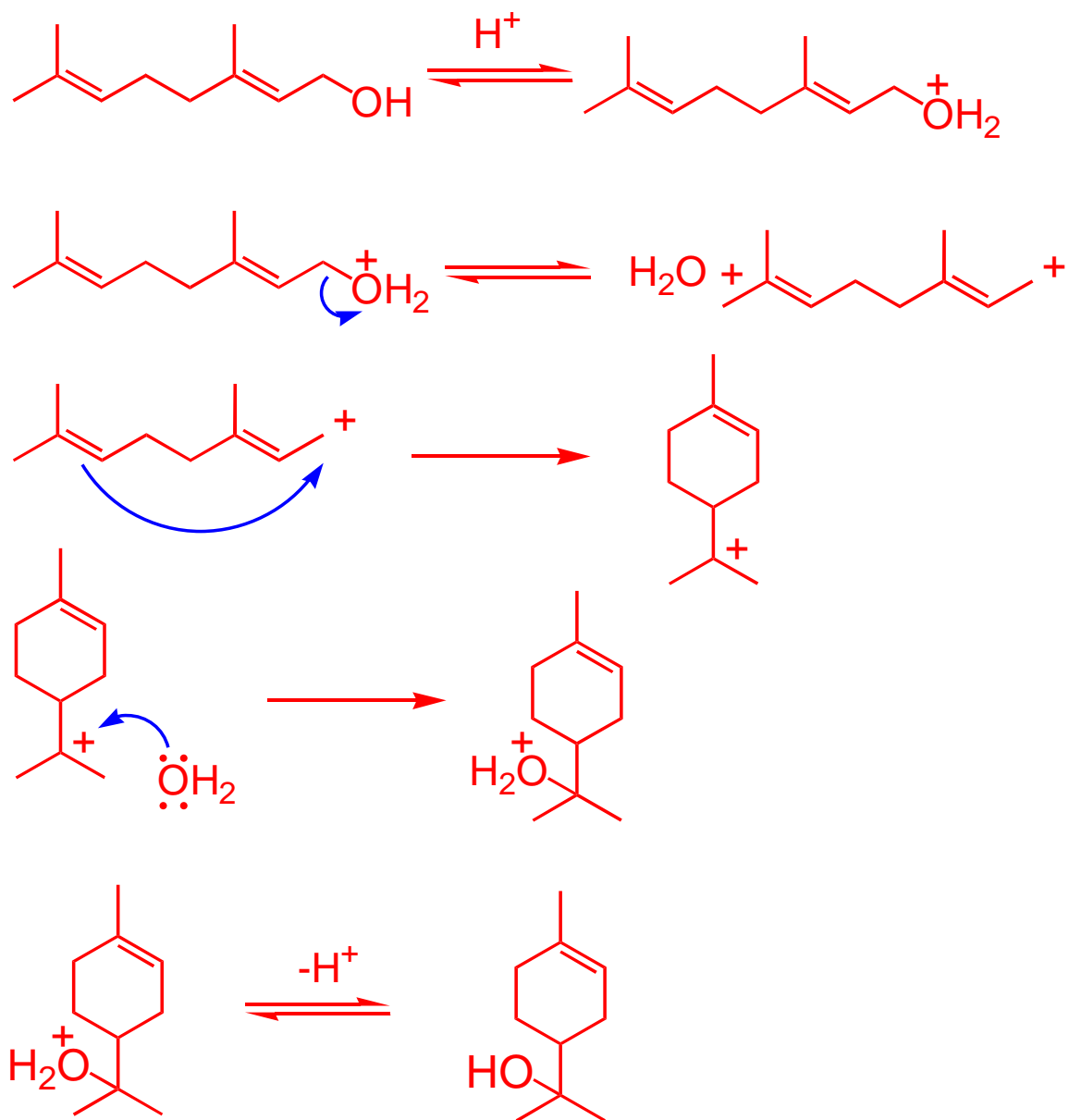
- i. CH_3O^- or CH_3CO_2^-
 CH_3O^-
- ii. NH_3 or NH_4^+
 NH_3
- d. Which $\text{S}_{\text{N}}2$ reaction of each pair would you expect to take place more rapidly in a protic solvent?
- i. $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl} + (\text{C}_6\text{H}_5)_3\text{N} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{N}^+(\text{C}_6\text{H}_5)_3 + \text{Cl}^-$
 or
 $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl} + (\text{C}_6\text{H}_5)_3\text{P} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{P}^+(\text{C}_6\text{H}_5)_3 + \text{Cl}^-$
 $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl} + (\text{C}_6\text{H}_5)_3\text{P} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{P}^+(\text{C}_6\text{H}_5)_3 + \text{Cl}^-$
- ii. $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl} + \text{CH}_3\text{O}^- \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{OCH}_3 + \text{Cl}^-$
 or
 $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl} + \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{OCH}_3 + \text{HCl}$
 $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl} + \text{CH}_3\text{O}^- \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{OCH}_3 + \text{Cl}^-$
- e. Propose a mechanistic explanation to account for the fact that $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$ reacts with 0.01 M NaCN in ethanol to yield primarily $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CN}$, whereas under the same conditions $(\text{CH}_3)_3\text{CCl}$ reacts to give primarily $(\text{CH}_3)_3\text{COCH}_2\text{CH}_3$.



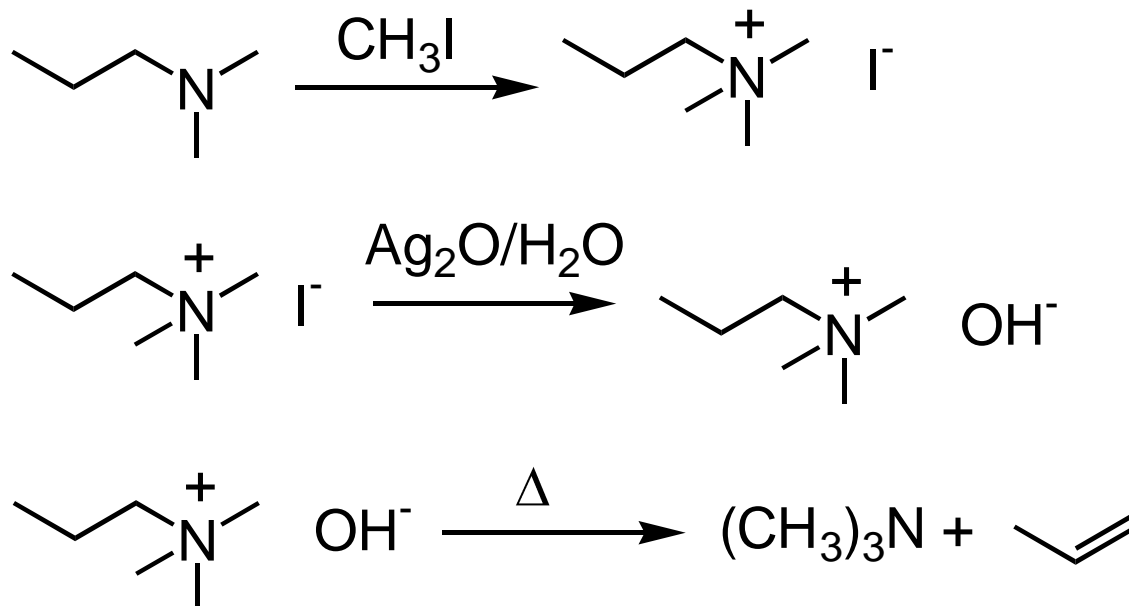


7. Propose a mechanism for the following transformation of nerol into α -terpineol:

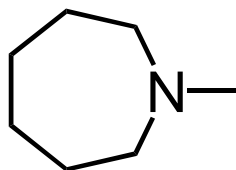




8. The Hofmann elimination of amines has been used to elucidate the structure of alkaloids. In this process the amine is first completely methylated with excess iodomethane and then treated with moist silver oxide (a source of OH^-) to produce the hydroxide salt. Heating degrades the salt to the alkene. Thus



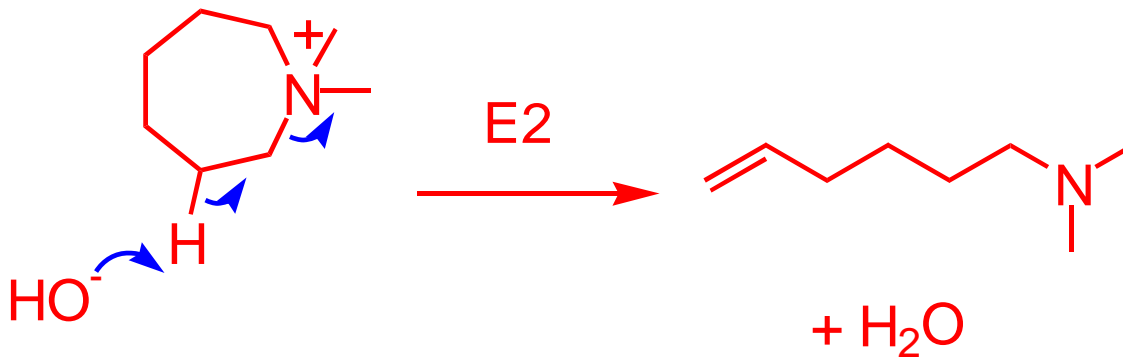
- a. Draw the final product of Hofmann elimination of *N*-methylazacycloheptane.



N-methylazacycloheptane

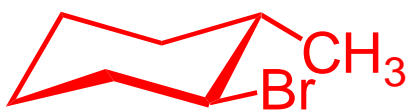


- b. Propose a mechanism for the last step leading to this product.

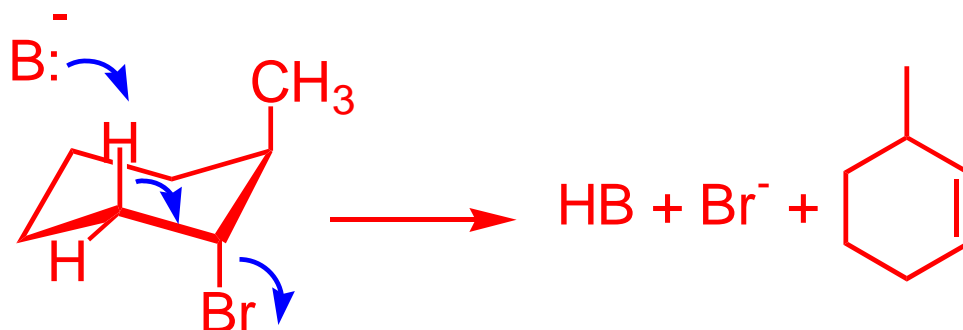
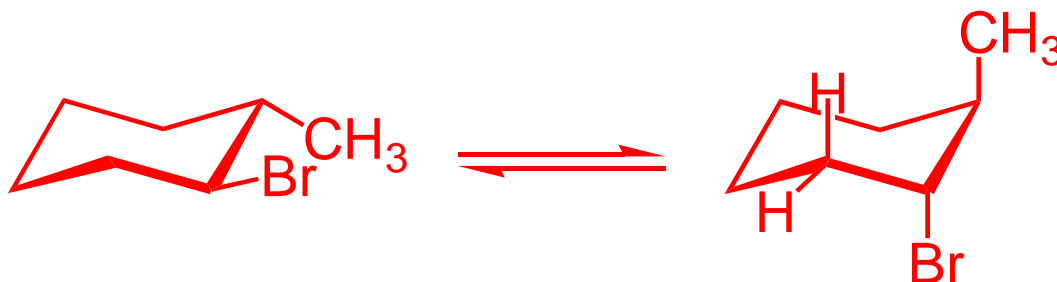


9. *trans*-1-Bromo-2-methylcyclohexane gives 3-methylcyclohexene on treatment with base and not the Saytzeff elimination product, 1-methylcyclohexene.

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



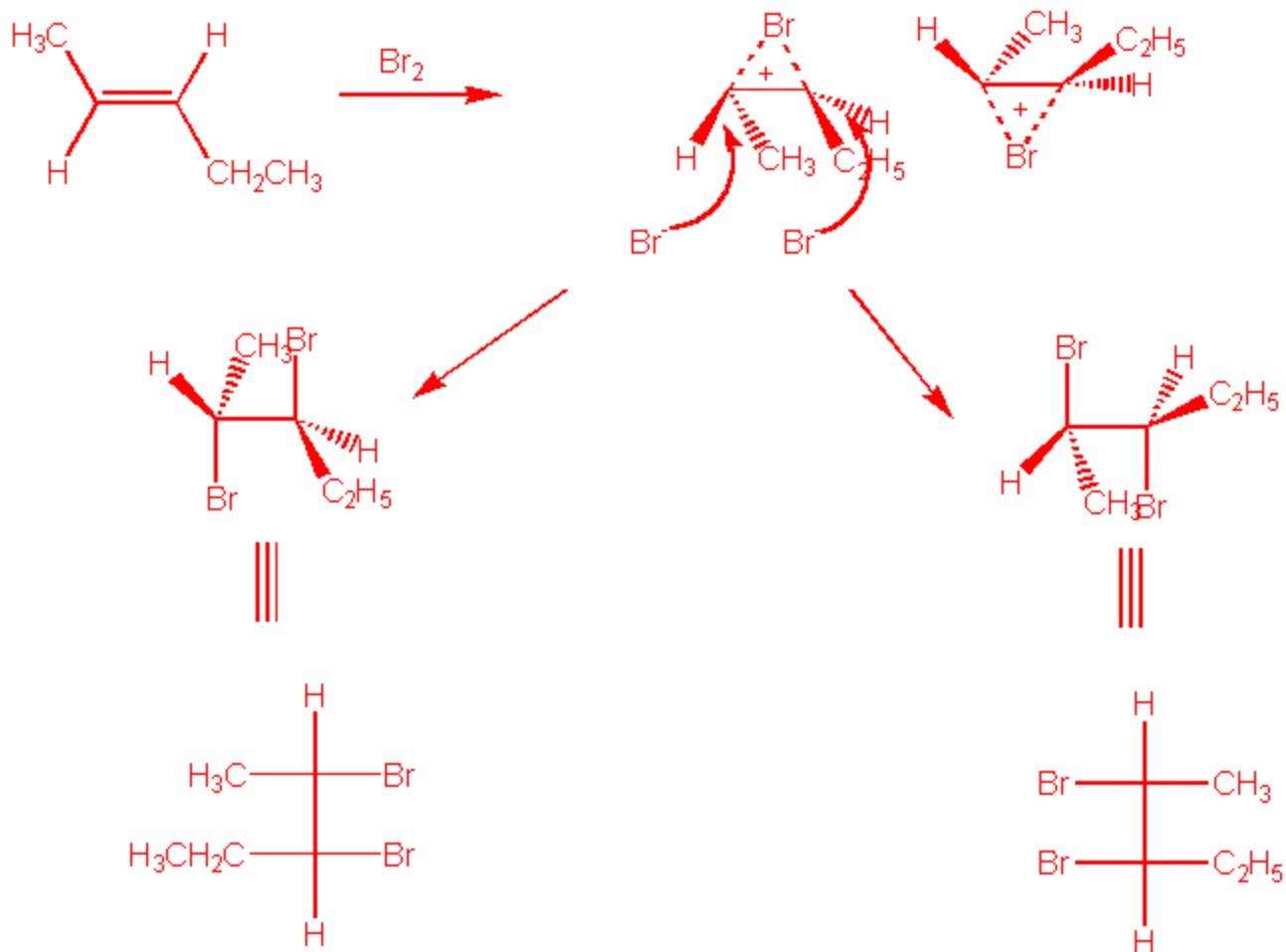
b. Propose a mechanism that explains the formation of 3-methylcyclohexene.



c. Why does the Saytzeff elimination product, 1-methylcyclohexene, not form?

The hydrogen on C-2 cannot be anti to the bromine.

10. Bromine reacts with (E)-2-pentene to give racemic mixture of (2R,3S)-2,3-dibromopentane and (2S,3R)-2,3-dibromopentane. Propose a mechanism that explains the formation of the racemic mixture.



11. Bisabolene, $\text{C}_{15}\text{H}_{24}$, is a terpene that is found in myrrh and oil of bergamot. There is no peak between 2100 and 2300 cm^{-1} in its IR spectrum. Catalytic hydrogenation gives a compound of formula $\text{C}_{15}\text{H}_{30}$.

a. How many units of unsaturation are present in bisabolene?

$$(2 \times 15 - 24 + 2)/2 = 4$$

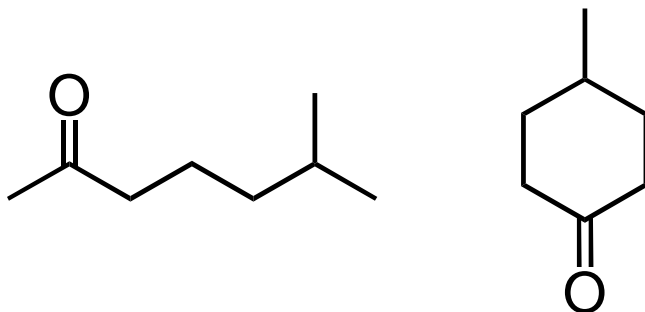
b. How many double bonds are present in bisabolene?

The hydrogenated product has $(2 \times 15 - 30 + 2)/2 = 1$ degree of unsaturation. Therefore there are 3 double bonds as there is no triple bond.

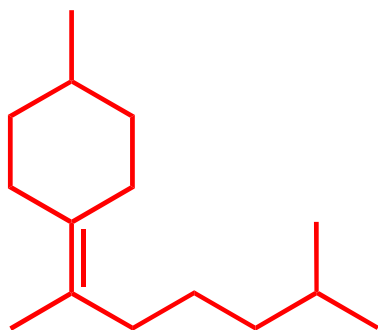
c. How many rings are present in bisabolene?

1

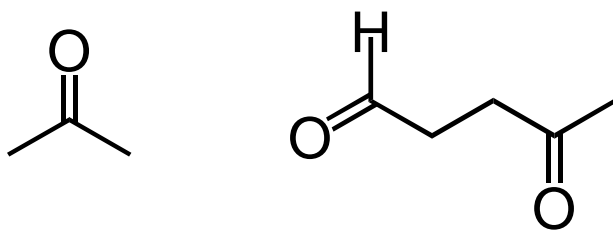
d. Partial hydrogenation of bisabolene gives compound "X", $C_{15}H_{28}$. Ozonolysis of compound "X" gives the following two compounds:



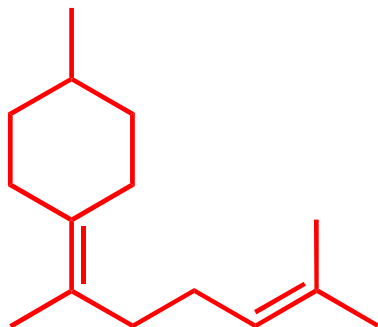
Draw the structure of compound "X".



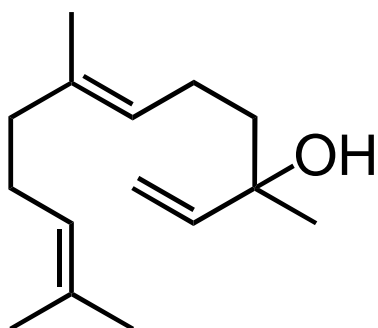
e. Ozonolysis of bisabolene that has NOT been hydrogenated gives, among other products, the following two compounds:



Compound "X" provides the carbon skeleton of bisabolene. This new ozonolysis data allows you to locate another double bond. Draw a structure which shows its position.

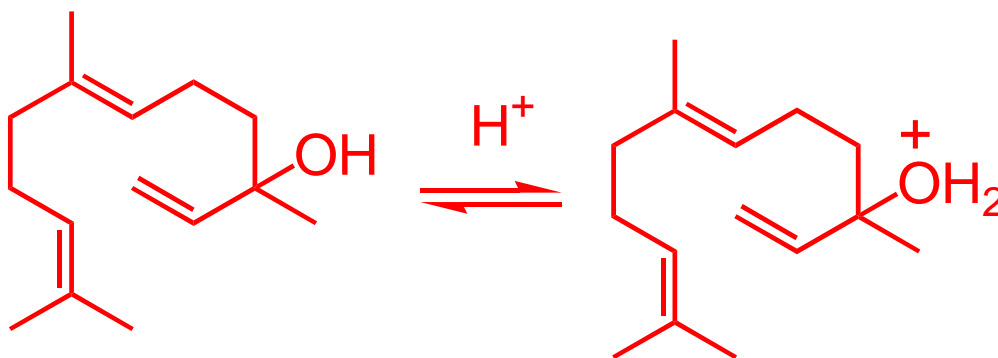


- f. Nerolidol, obtained from the flowers of bitter orange, undergoes acid-catalyzed cyclization to yield bisabolene.

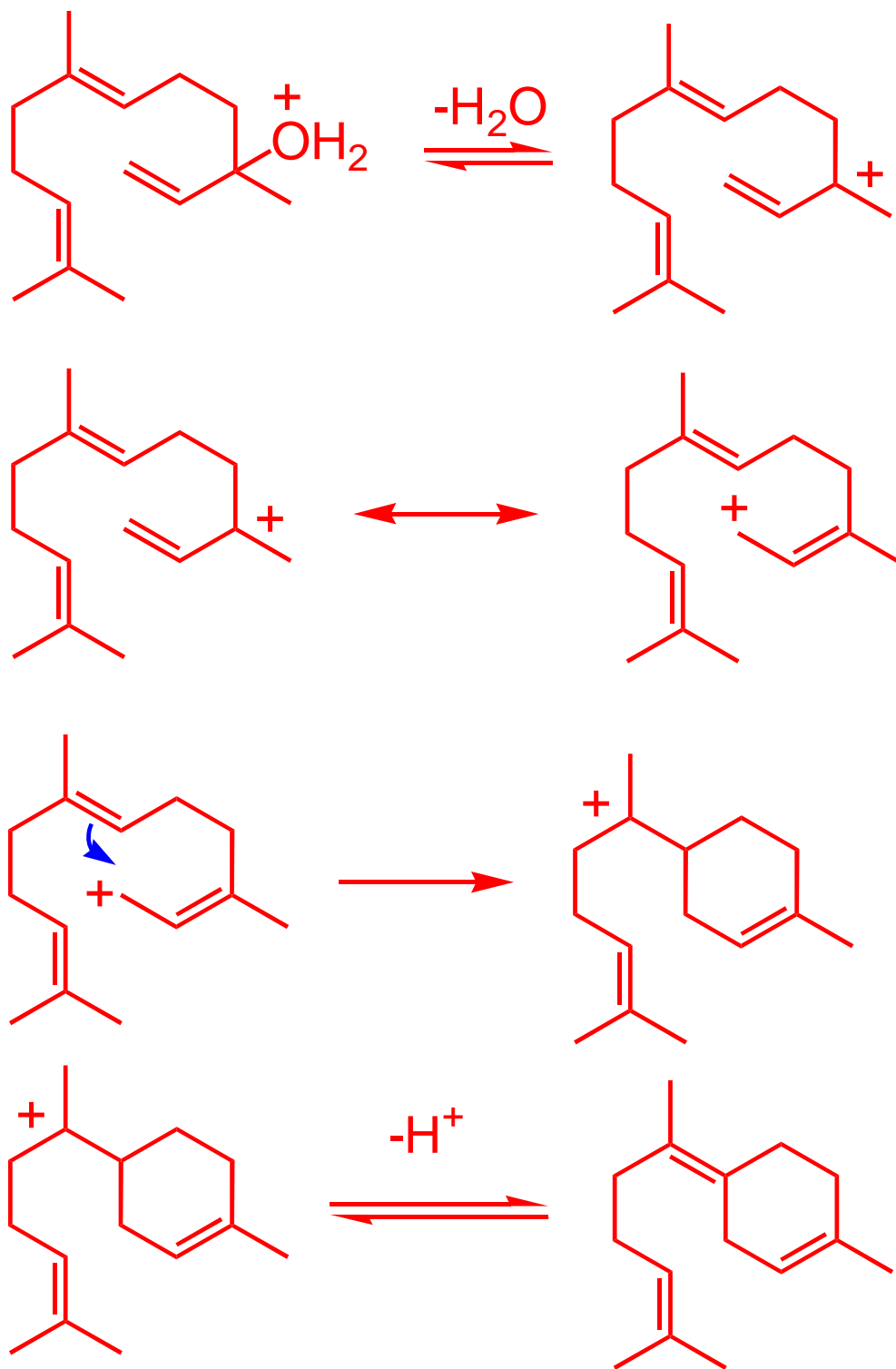


nerolidol

Draw the first step in the mechanism.



- g. Complete the mechanism.



h. Draw the structure of bisabolene.

