

Chemistry Department

University of Alberta

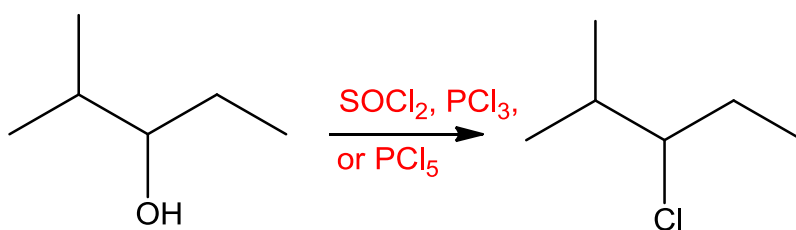
CHEM 261

Final Exam

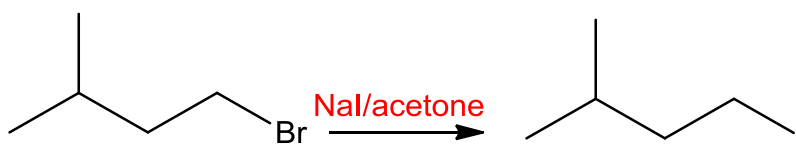
May 25, 2012

1. What reagents would you use to effect the following conversions? (15 points)

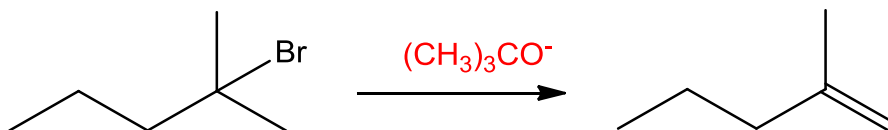
a.



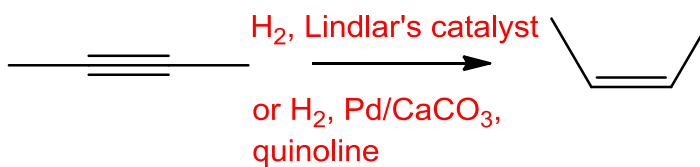
b.



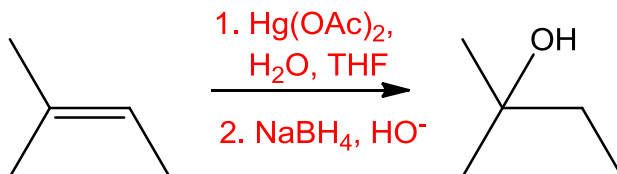
c.



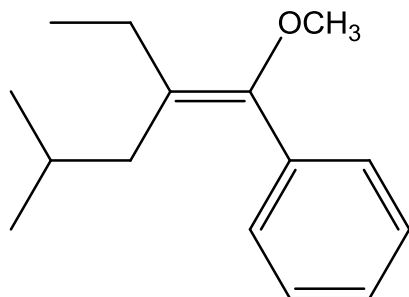
d.



e.

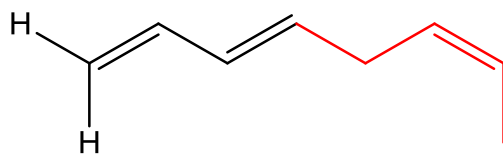
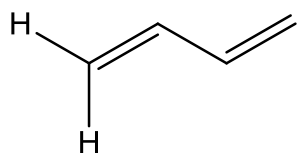


2. Name the following compound by the IUPAC system. The name must indicate the stereochemistry of the compound. (4 points)



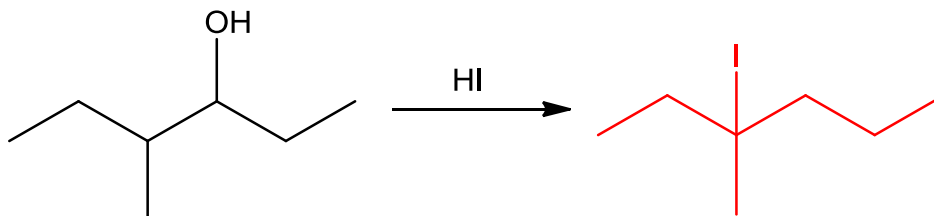
(E)-2-ethyl-1-methoxy-4-methyl-1-phenyl-1-pentene  
or (E)-2-ethyl-1-methoxy-4-methyl-1-phenylpent-1-ene

3. Complete the following partial structure of (3E,6Z)-1,3,6-octatriene: (4 points)

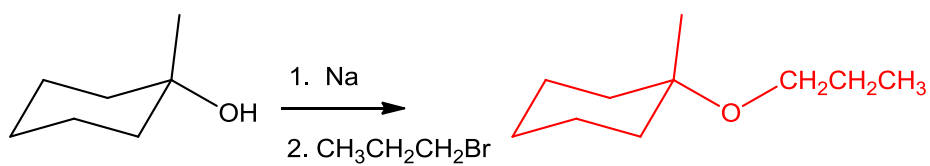


4. Give the structure(s) of the major organic products of the following reactions: (15 points)

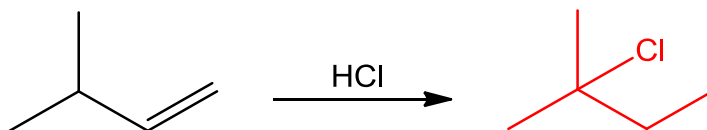
a.



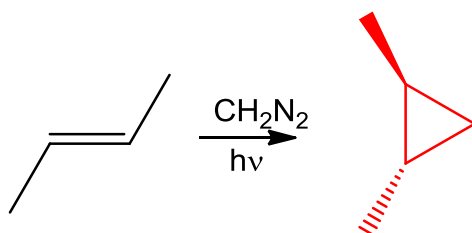
b.



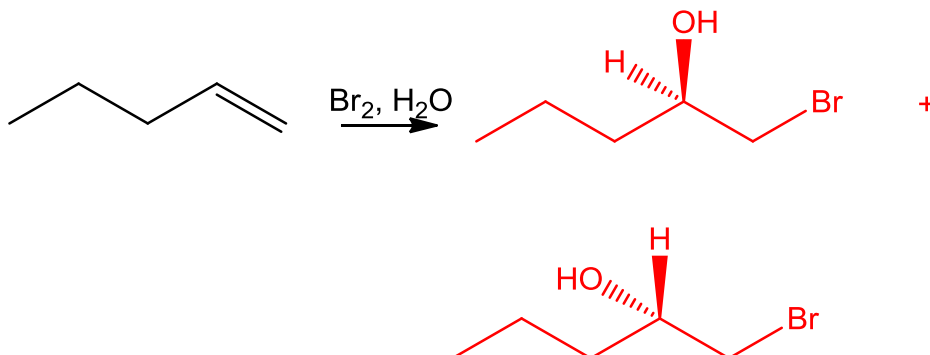
c.



d.

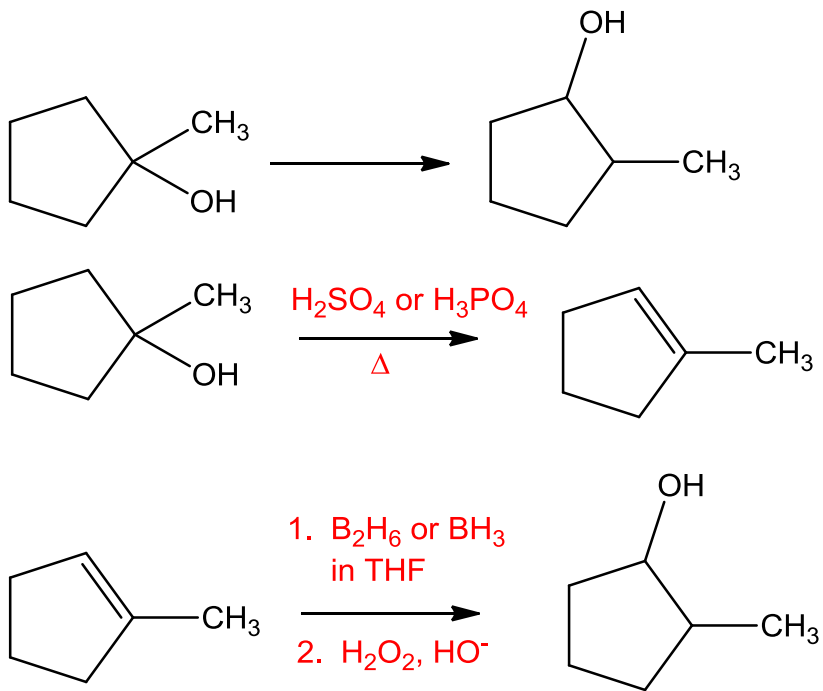


e.

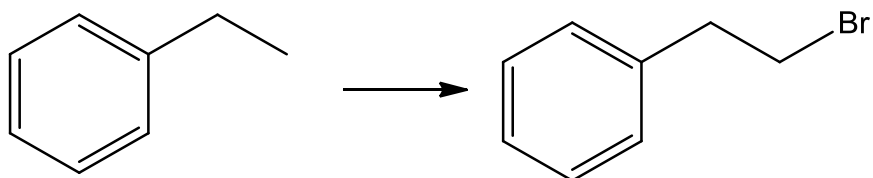


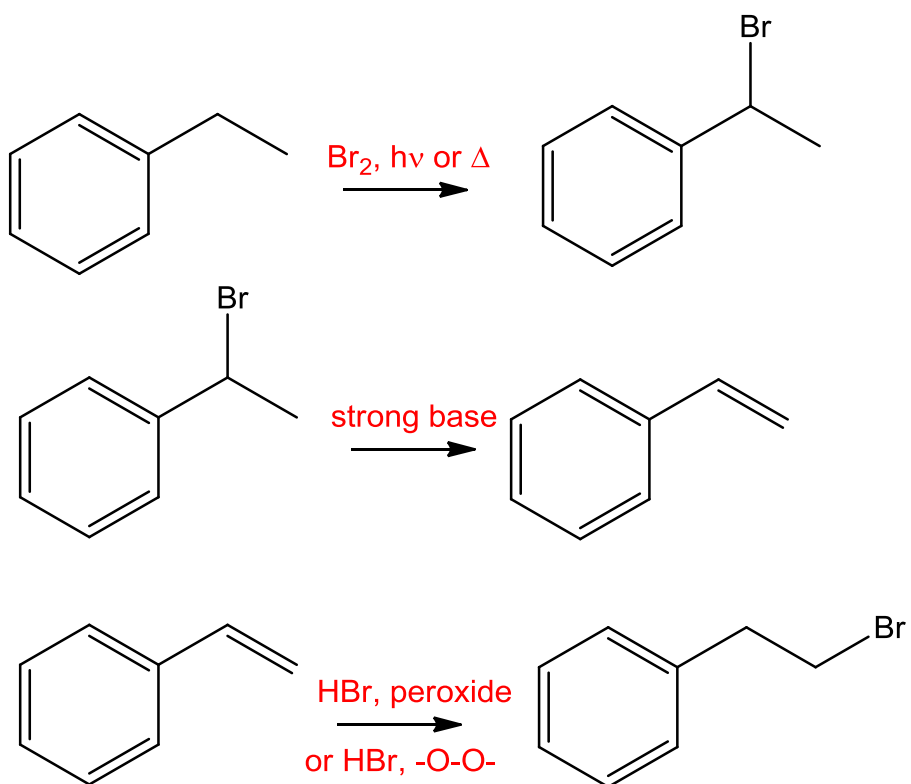
5. Provide a synthetic pathway for the following transformations. Begin your synthesis with the indicated starting material. (27 points)

a.

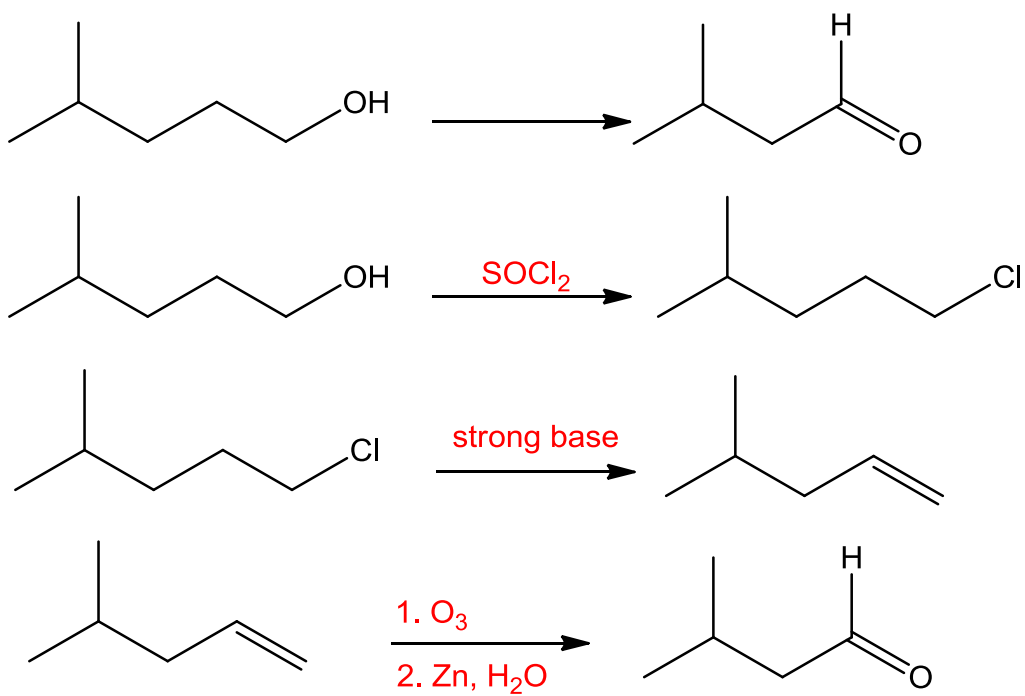


b.





c.



6.

a. Select the member of each pair of compounds that will be the more reactive nucleophile in a protic solvent: (3 points)

i.  $\text{HO}^-$  or  $\text{HS}^-$

$\text{HS}^-$

ii.  $\text{CH}_3\text{CO}_2^-$  or  $\text{CH}_3\text{CO}_2\text{H}$

$\text{CH}_3\text{CO}_2^-$

iii.  $\text{NH}_3$  or  $\text{PH}_3$

$\text{PH}_3$

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

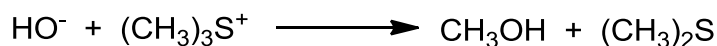
i. 1-bromopentane or 2-bromopentane

1-bromopentane

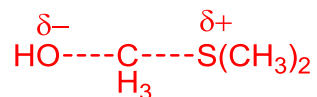
ii.  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$  or  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{I}$

$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{I}$

c. Explain why increasing the solvent polarity causes a large decrease in the rate of the  $\text{S}_{\text{N}}2$  attack by hydroxide ion on the trimethylsulfonium ion,  $(\text{CH}_3)_3\text{S}^+$ . (3 points)



The two charged reagents give two uncharged products. Therefore both charges are beginning to disappear in the transition state:



A polar solvent forms stronger ion – dipole bonds with the full charges of the reactants than with the diminished charges in the transition state thereby stabilizing the reactants to a greater degree.  $E_{\text{a}}$  is increased and the reaction is slowed.

d. Select the member of each pair of compounds that will react faster by an  $S_N1$  mechanism: (2 points)

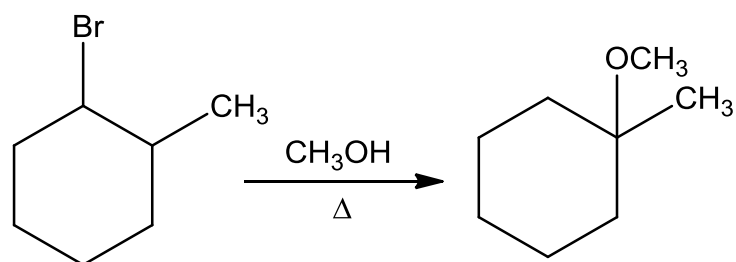
i.  $(CH_3)_3CBr$  or  $(CH_3)_3CI$

$(CH_3)_3CI$

ii.  $CH_3CH_2CHBrCH_3$  or  $CH_3CH_2CH_2CH_2Br$

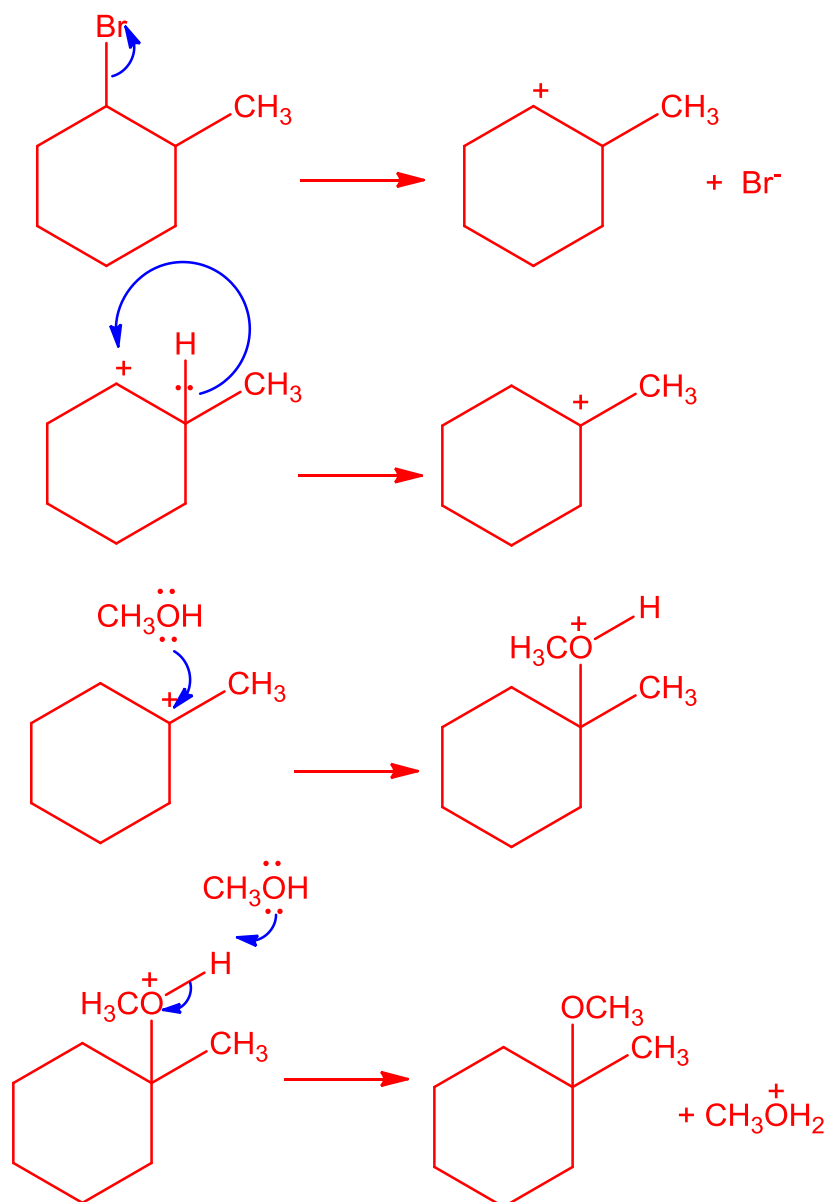
$CH_3CH_2CHBrCH_3$

7. The solvolysis of 1-bromo-2-methylcyclohexane in methanol gives a number of major products including 1-methoxy-1-methylcyclohexane:



Draw the most likely mechanism for this reaction. (Don't forget the curved arrows). (12 points)

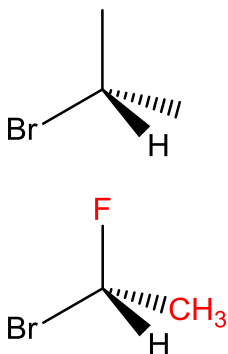




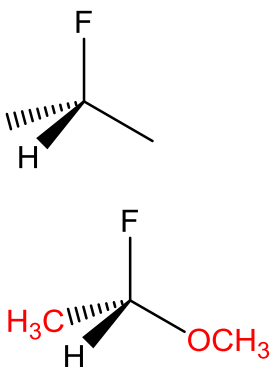
I.D. No. \_\_\_\_\_

8. Under appropriate conditions, (S)-1-bromo-1-fluoroethane reacts with sodium methoxide, ( $\text{NaOCH}_3$ ), to give pure (S)-1-fluoro-1-methoxyethane.

a. Complete the following partial structure of (S)-1-bromo-1-fluoroethane: (2 points)



b. Complete the following partial structure of (S)-1-fluoro-1-methoxyethane: (2 points)



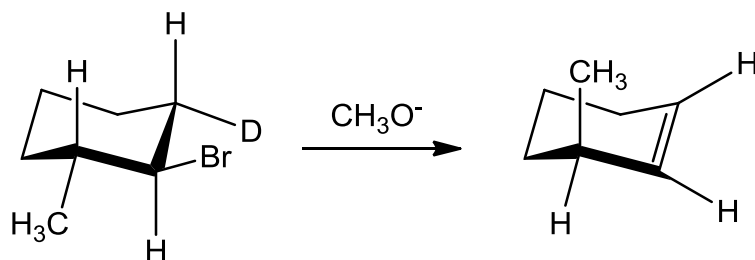
c. Draw the most likely mechanism for this reaction. (Don't forget the curved arrows). (3 points)



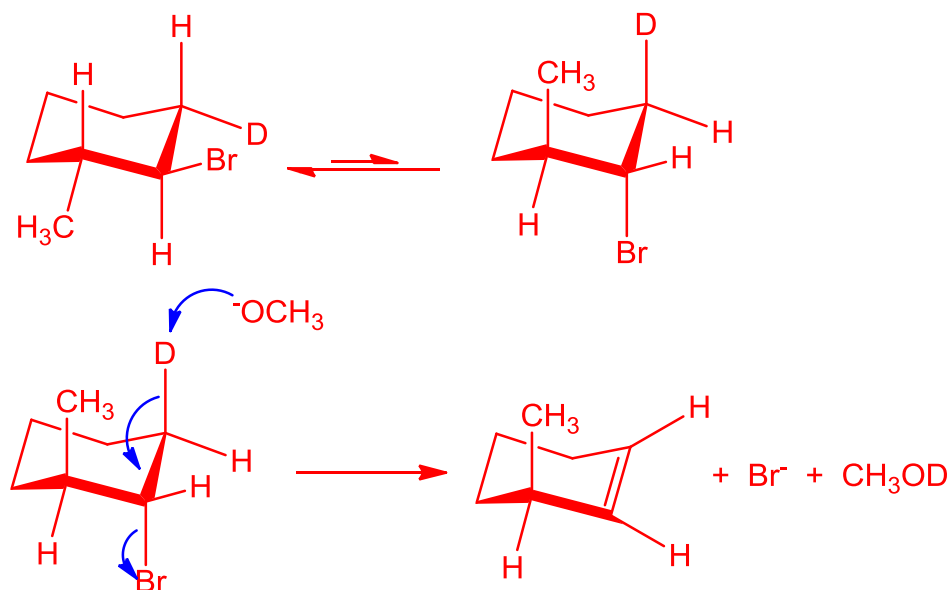
d. Why is the bromide replaced rather than the fluoride? (1 point)

It is a better leaving group as it is a weaker base. (HBr is a stronger acid than HF)

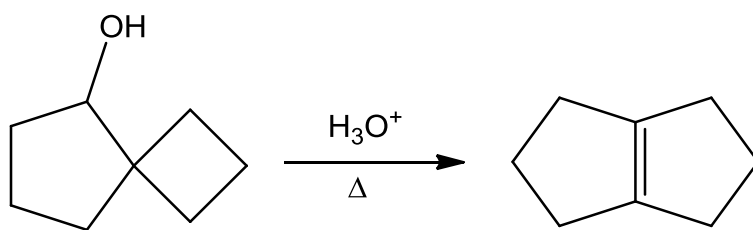
9. The following deuterated 1-bromo-2-methylcyclohexane undergoes dehydrobromination to form only the one cyclohexene shown below:

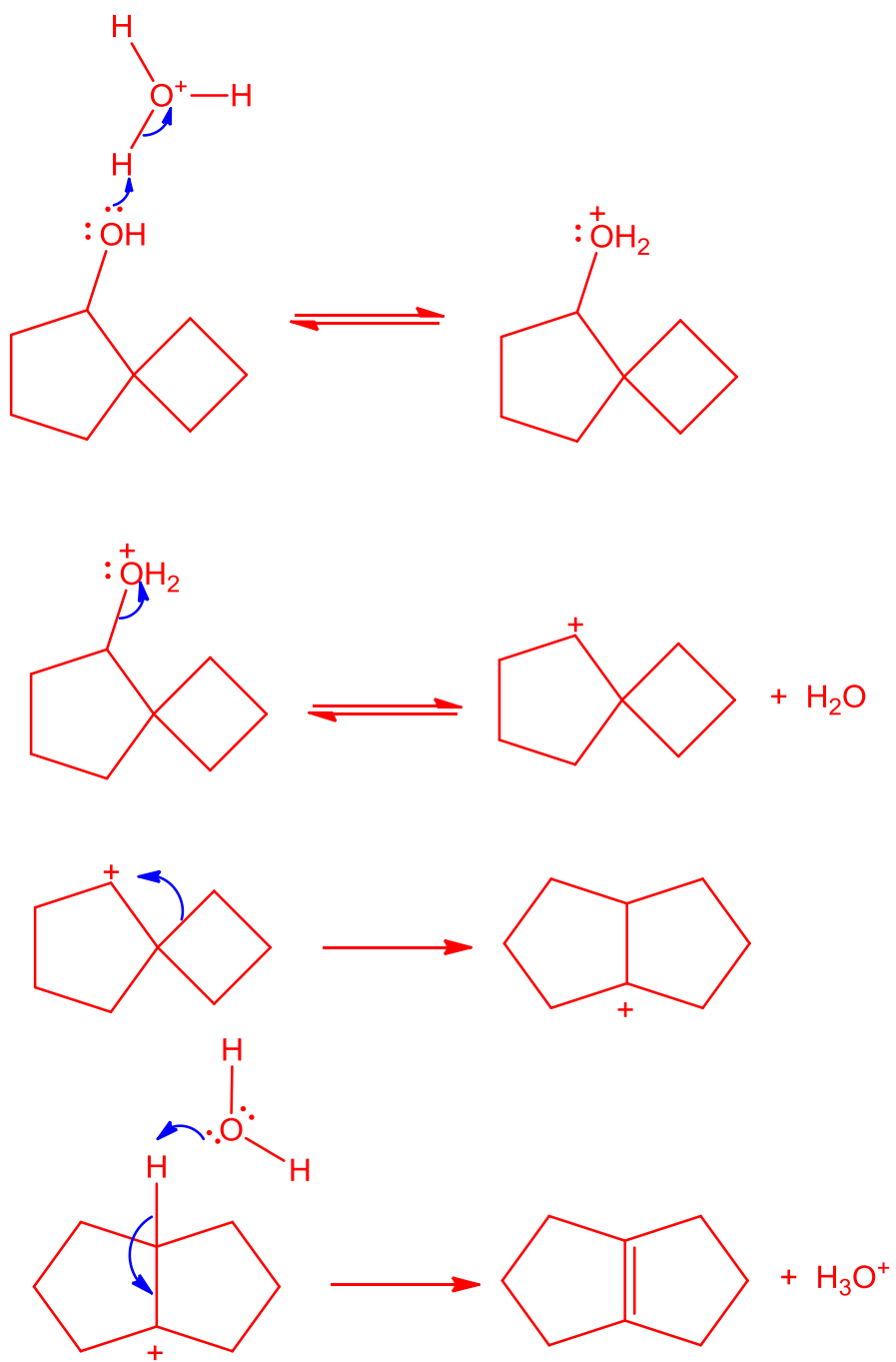


Draw the most likely mechanism for this reaction. (Don't forget the curved arrows). (6 points)



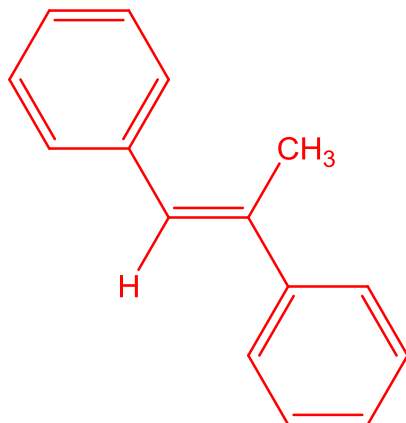
10. Draw the most likely mechanism for the following reaction: (Don't forget the curved arrows). (12 points)



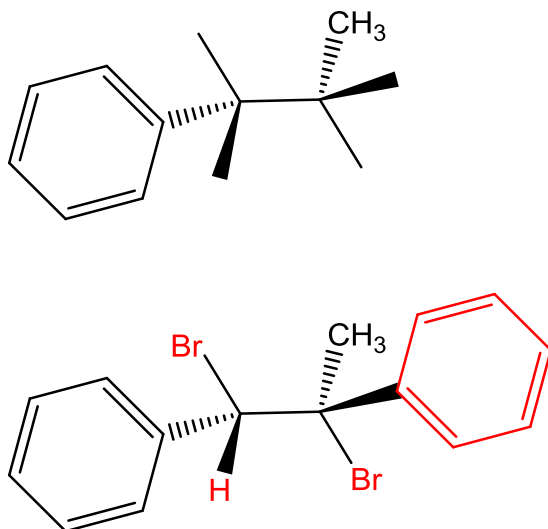


11. Bromine in a tetrachloromethane solution reacts with (E)-1,2-diphenylpropene to a racemic mixture of (1S,2R)-1,2-dibromo-1,2-diphenylpropane and its enantiomer.

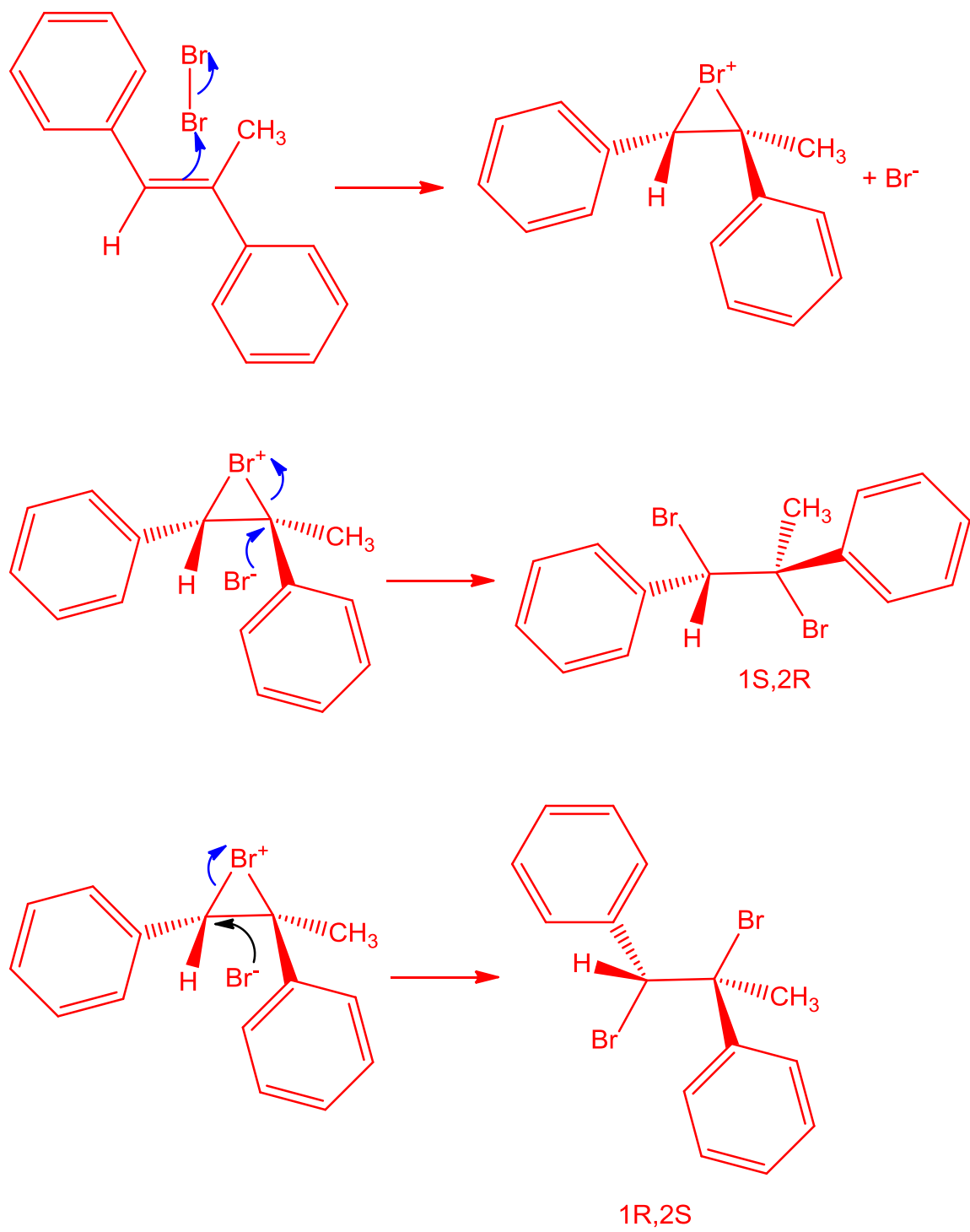
a. Draw the structure of (E)-1,2-diphenylpropene: (1 points)



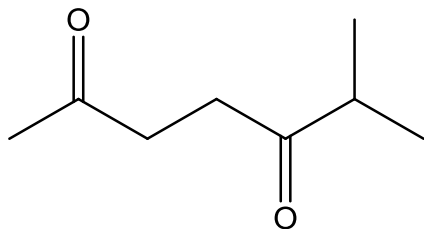
b. Draw the structure of (1S,2R)-1,2-dibromo-1,2-diphenylpropane using the following partial structure: (4 points)



c. Draw a mechanism that explains the stereochemistry observed in this bromination. (9 points)



12.  $\alpha$ -Terpinene, a terpene found in coriander oil, has the formula  $C_{10}H_{16}$  and is known not to contain any triple bond. On catalytic hydrogenation,  $\alpha$ -terpinene is converted to *p*-menthane,  $C_{10}H_{20}$ . Ozonolysis of  $\alpha$ -terpinene yields two products, one of which is the following diketone:



- a. How many units of unsaturation are present in  $\alpha$ -terpinene? (1 point)

$$(2 \times 10 - 16 + 2)/2 = 3$$

- b. How many double bonds are there in  $\alpha$ -terpinene? (1 point)

2

- c. What is the structure of  $\alpha$ -terpinene? (3 points)

