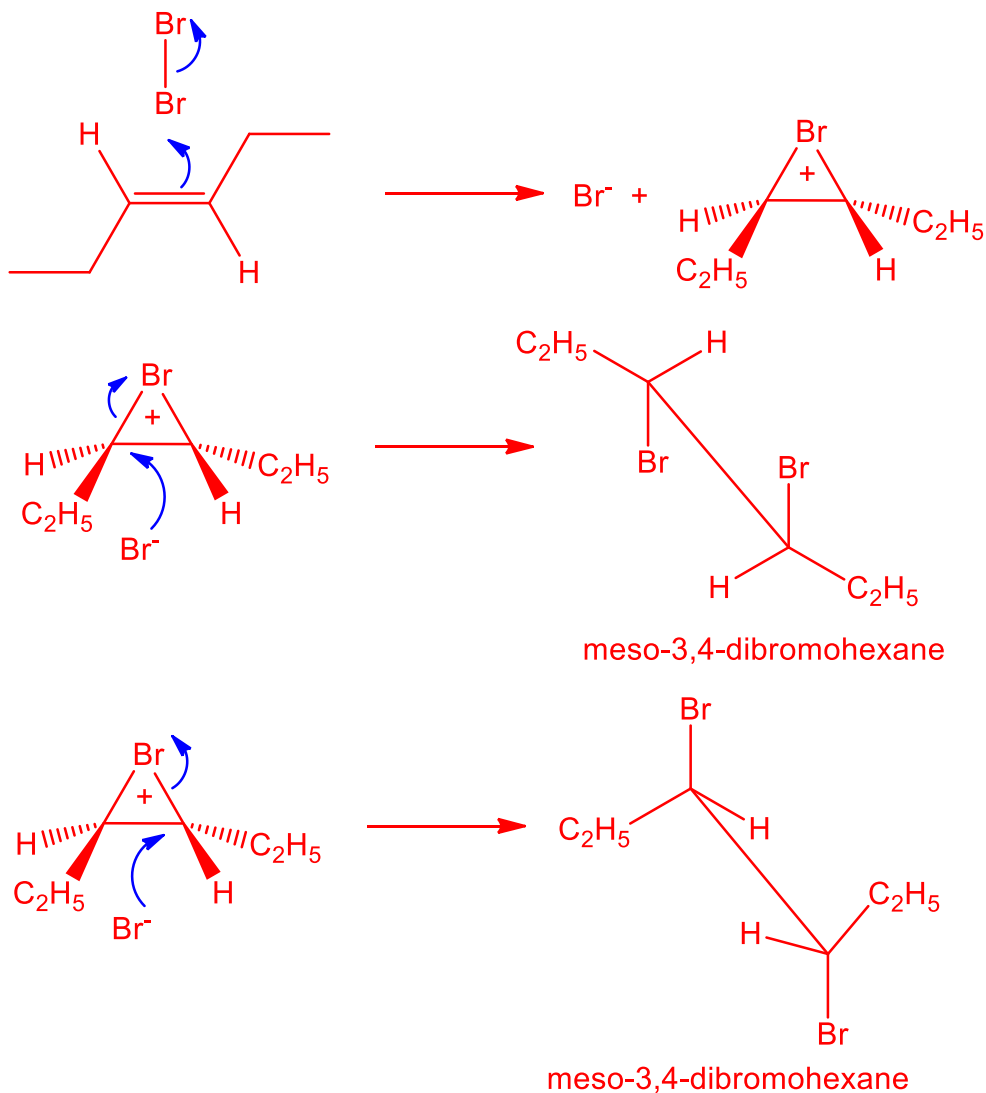


Exercise 14: - Reactions of alkenes and alkynes

1. In carbon tetrachloride solution, bromine adds to (*E*)-3-hexene to yield meso 3,4-dibromohexane. Propose a mechanism that explains this behavior.

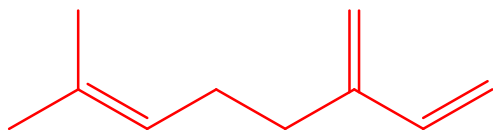


2. Myrcene a fragrant component found in bayberry wax, has the formula C₁₀H₁₆ and is known not to contain any triple bond. On catalytic hydrogenation, myrcene is converted to 2,6-dimethyloctane. Ozonolysis of myrcene followed by treatment with zinc and water yields 2 mol of formaldehyde, HCHO, 1 mol of acetone (CH₃COCH₃) and a third compound with formula C₅H₆O₃.

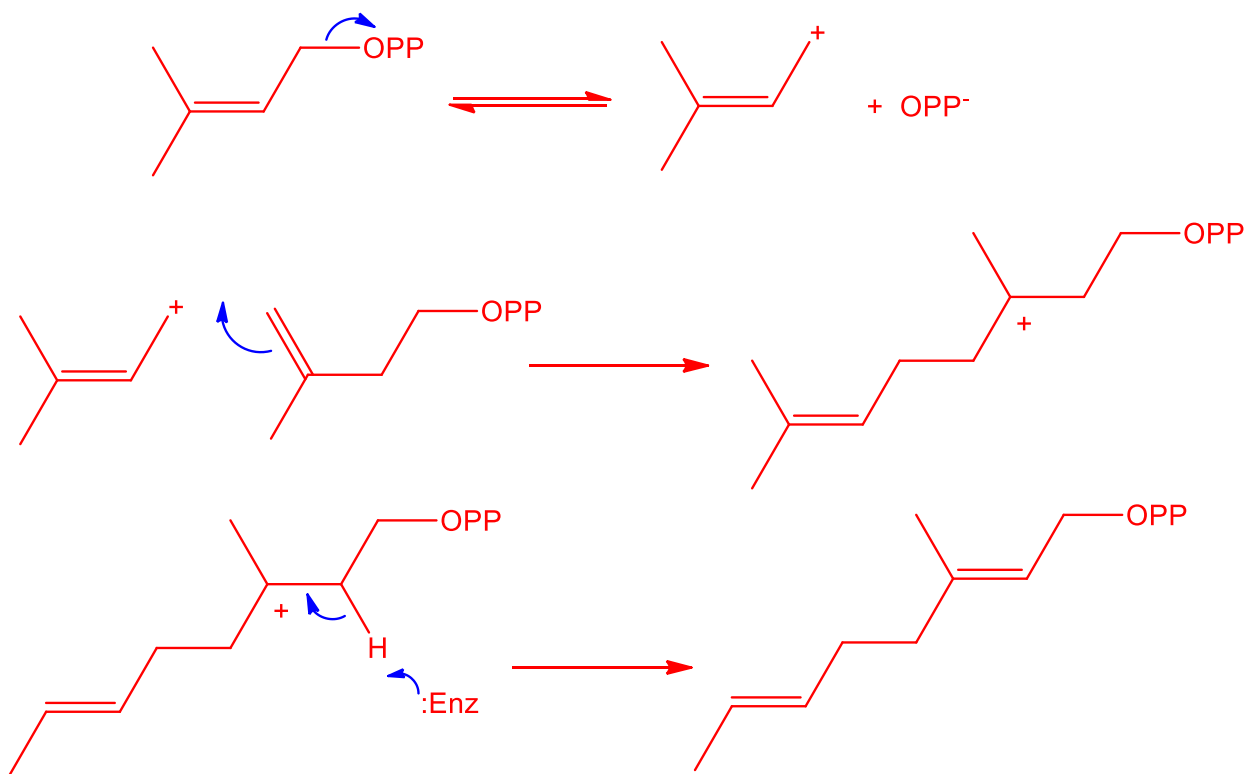
- a. How many units of unsaturation are present in myrcene?

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

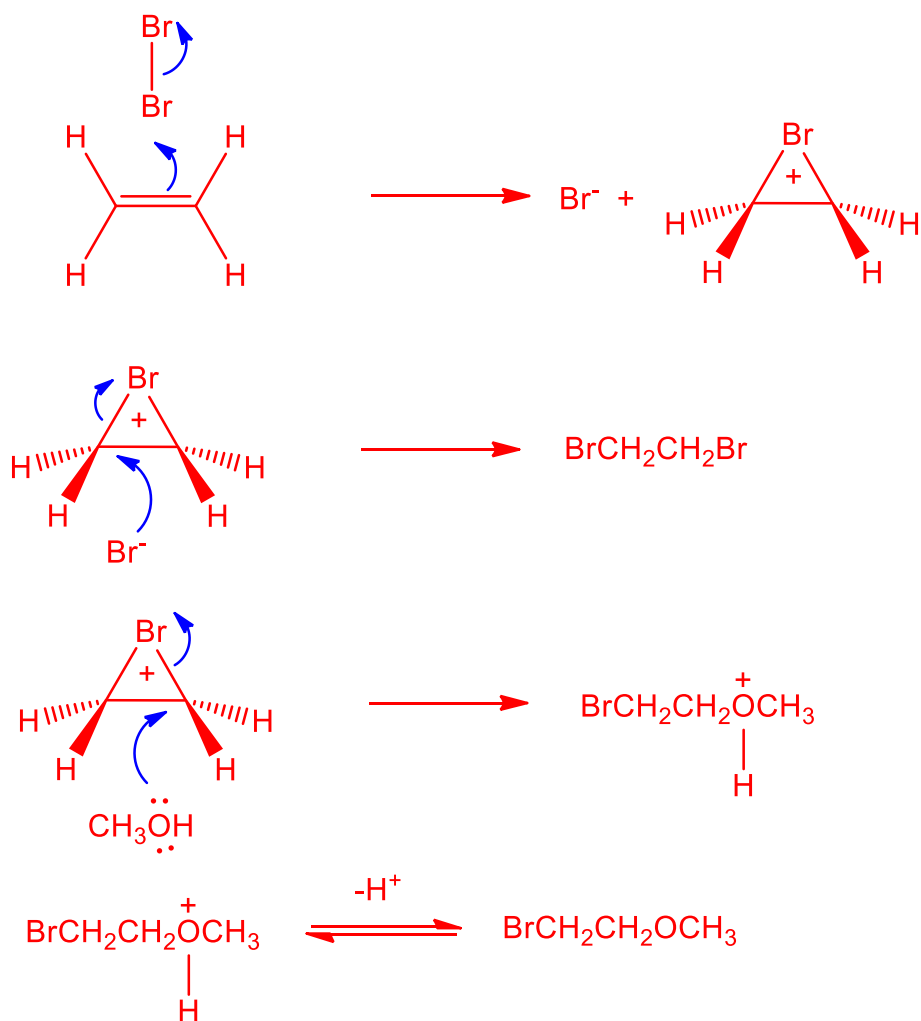
- b. What is the structure of myrcene?



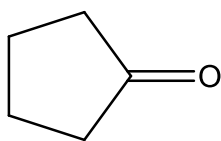
3. At the beginning of the biogenesis of squalene isopentenyl pyrophosphate, $\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{OPP}$, is enzymatically isomerized to dimethylallyl pyrophosphate, $(\text{CH}_3)_2\text{C}=\text{CHCH}_2\text{OPP}$. These two compounds then react together to yield geranyl pyrophosphate, $(\text{CH}_3)_2\text{C}=\text{CHCH}_2\text{CH}_2(\text{CH}_3)\text{C}=\text{CHCH}_2\text{OPP}$. Assuming that the weakly basic pyrophosphate anion is, like the protonated hydroxyl group, a good leaving group, $\text{R-OPP} \rightarrow \text{R}^+ + \text{OPP}^-$ suggest a mechanism by which geranyl pyrophosphate might be formed.



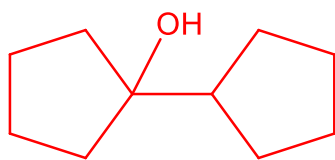
4. In methanol solution, bromine adds to ethene to yield not only 1,2-dibromoethane but also $\text{Br-CH}_2\text{-CH}_2\text{-O-CH}_3$. Write a mechanism that explains this behavior.



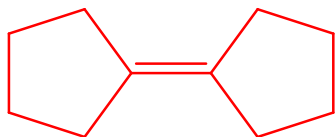
5. Compound "A", $\text{C}_{10}\text{H}_{18}\text{O}$, reacts with dilute H_2SO_4 at 250°C to yield a mixture of two alkenes, $\text{C}_{10}\text{H}_{16}$. The major product, "B", gives cyclopentanone, as the sole product on ozonolysis:



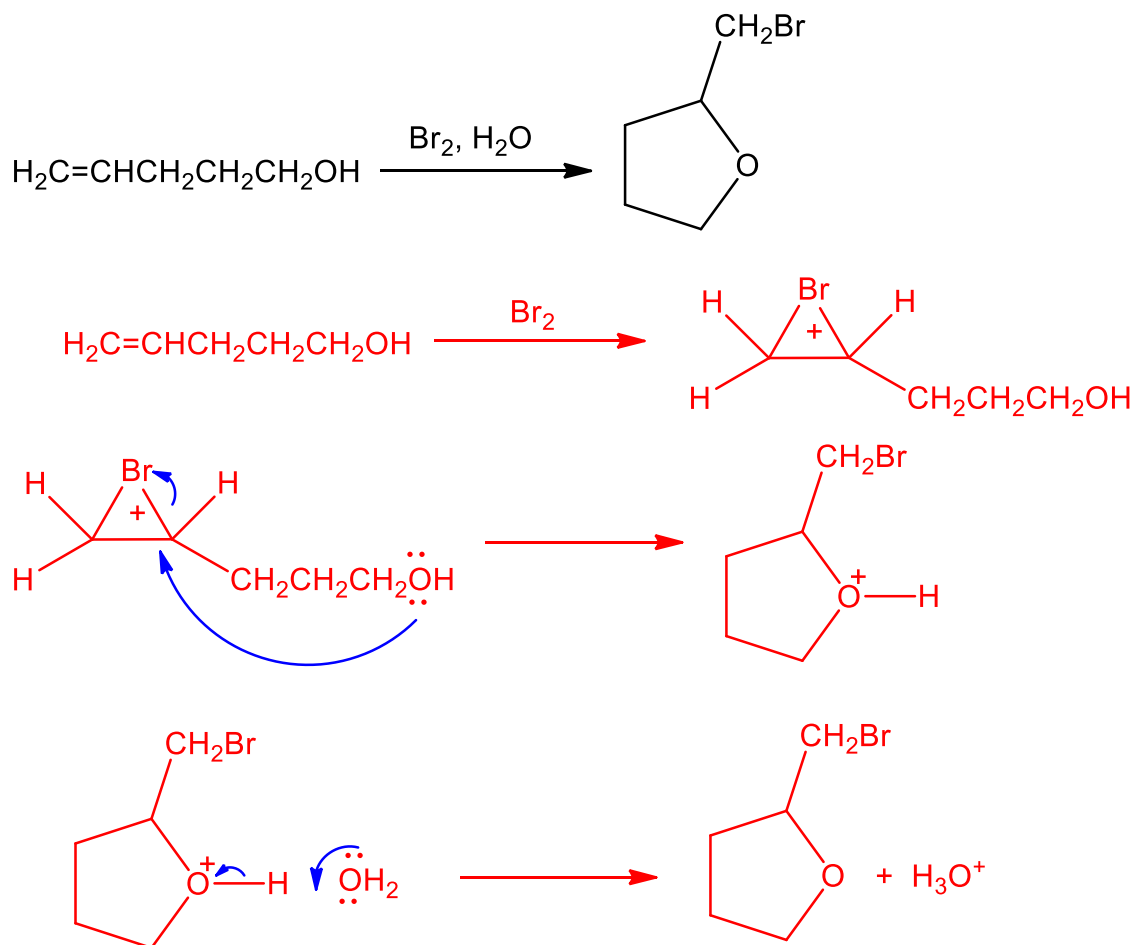
a. What is the structure of "A"?



b. What is the structure of "B"?

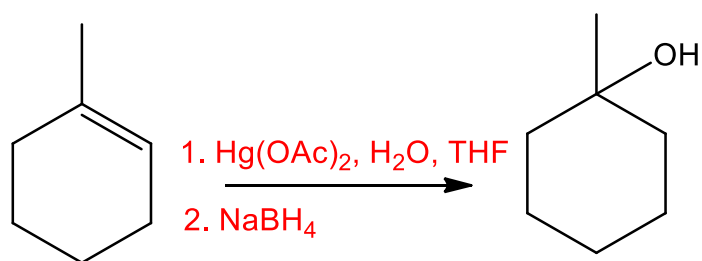


6. Propose a mechanism for the following reaction:

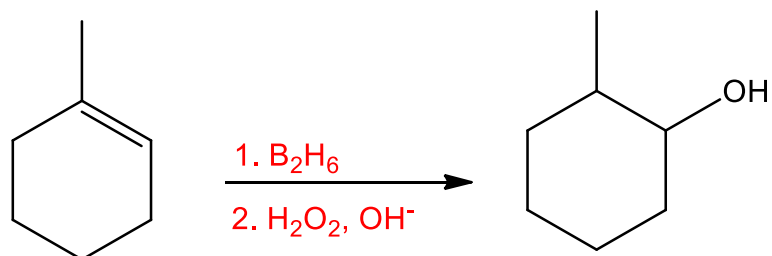


7. Starting from 1-methylcyclohexene, propose a synthesis for each of the following:

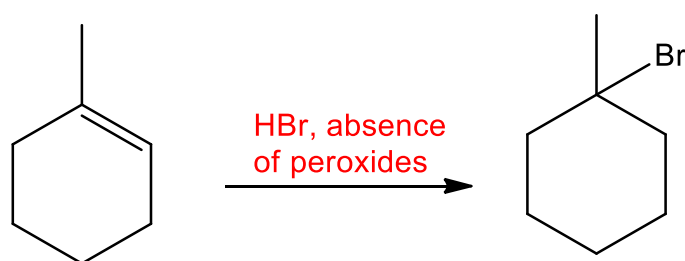
a. 1-methylcyclohexanol



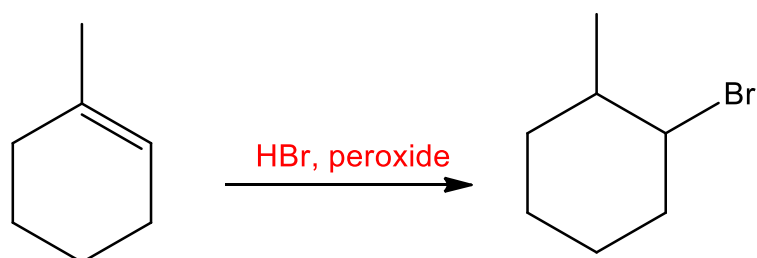
b. 2-methylcyclohexanol



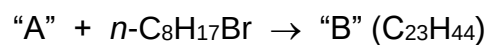
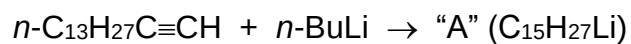
c. 1-bromo-1-methylcyclohexane

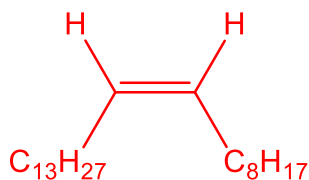


d. 1-bromo-2-methylcyclohexane

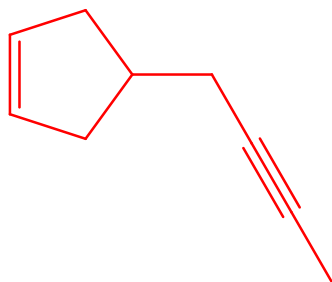


8. Muscalure is the sex pheromone of the common house fly. On the basis of the following synthesis, give the structure of muscalure:





9. Hydrocarbon "A", C_9H_{12} , absorbs three equivalents of H_2 on catalytic hydrogenation. "A" forms two isomeric ketones on treatment with aqueous H_2SO_4 /mercuric ion. Oxidation of "A" with $KMnO_4$ gives a mixture of ethanoic acid, CH_3CO_2H , and acid $CH(CH_2CO_2H)_3$. What is the structure of "A"?



10. Compound "A", C_9H_{12} , absorbs three equivalents of H_2 on catalytic hydrogenation. Ozonolysis gives cyclohexanone and other products. "A" reacts with $NaNH_2$ in liquid ammonia followed by CH_3I to give compound "B", $C_{10}H_{14}$. What is the structure of "A"?

