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 $C_{10}H_{16}$ 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 (CH_3COCH_3) and a third compound with formula $C_5H_6O_3$.

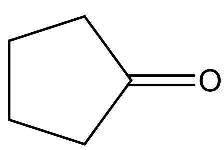
   a. How many units of unsaturation are present in myrcene?

   b. What is the structure of myrcene?

3. At the beginning of the biogenesis of squalene isopentenyl pyrophosphate, $CH_2{=}C(CH_3)CH_2CH_2OPP$, is enzymatically isomerized to dimethylallyl pyrophosphate, $(CH_3)_2C{=}CHCH_2OPP$. These two compounds then react together to yield geranyl pyrophosphate, $(CH_3)_2C{=}CHCH_2CH_2(CH_3)C{=}CHCH_2OPP$. Assuming that the weakly basic pyrophosphate anion is, like the protonated hydroxyl group, a good leaving group, $R\text{-}OPP \rightarrow R^+ + OPP^-$ 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 $Br\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH_3$. Write a mechanism that explains this behavior.

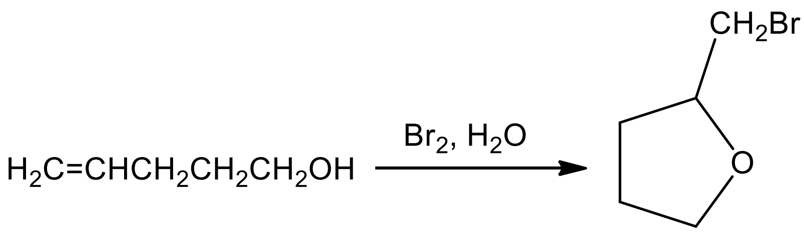
5. Compound "A", $C_{10}H_{18}O$, reacts with dilute H_2SO_4 at 250C to yield a mixture of two alkenes, $C_{10}H_{16}$. The major product, "B", gives cyclopentanone, as the sole product on ozonolysis:



   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:

    n-$C_{13}H_{27}C{\equiv}CH$ + *n*-BuLi $\rightarrow$ "A" ($C_{15}H_{27}Li$)

    "A" + *n*-$C_8H_{17}Br$ $\rightarrow$ "B" ($C_{23}H_{44}$)

    "B" + H_2, Lindlar catalyst $\rightarrow$ muscalure ($C_{23}H_{46}$)

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"?