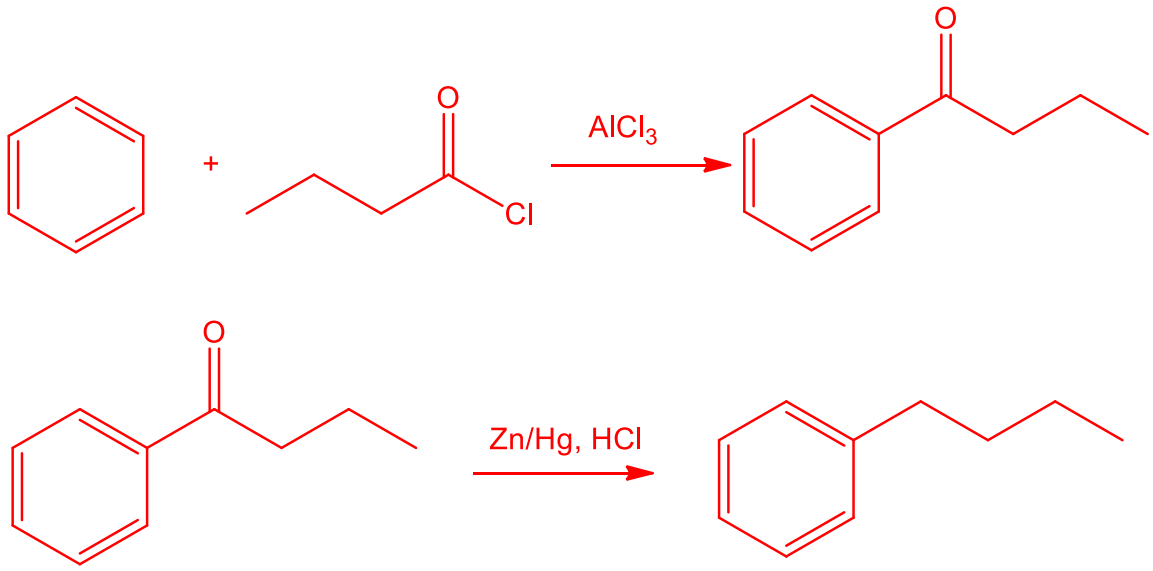
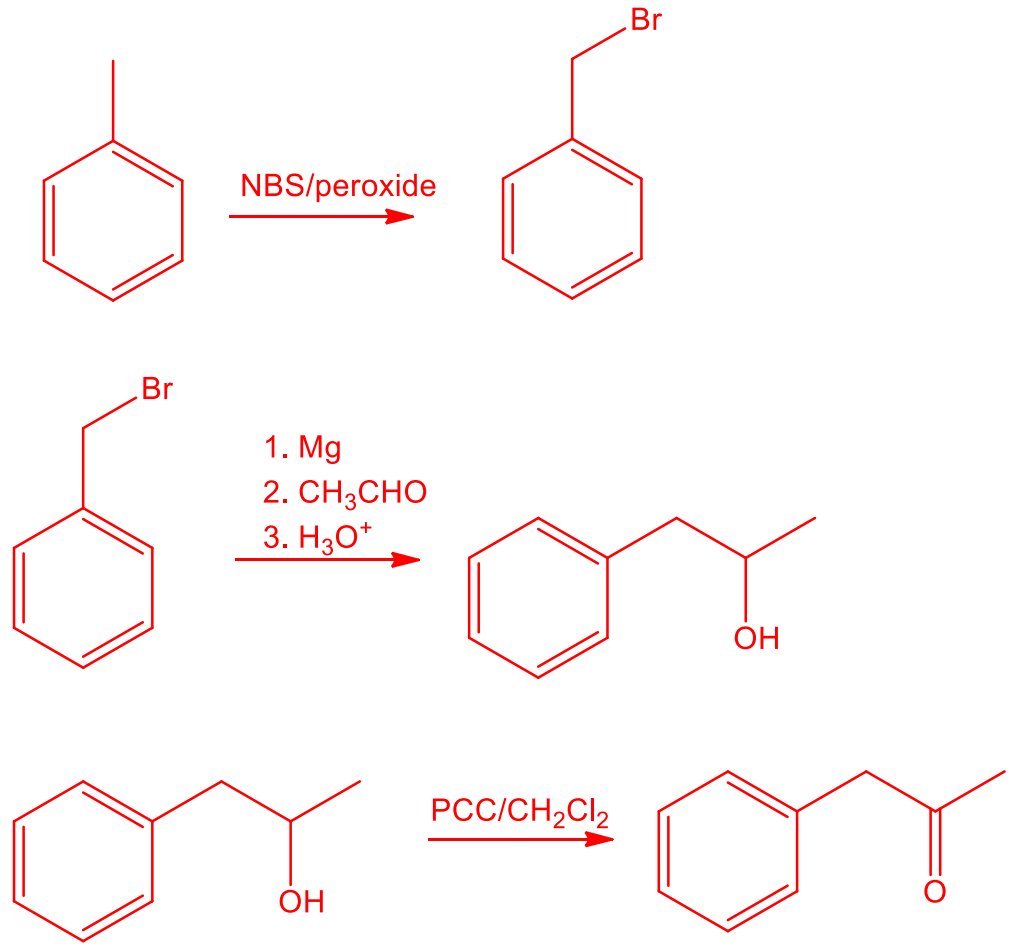
Problem Set 7 – Reactions of aldehydes and ketones

1. Outline a synthesis of the following compounds starting from either benzene or toluene:

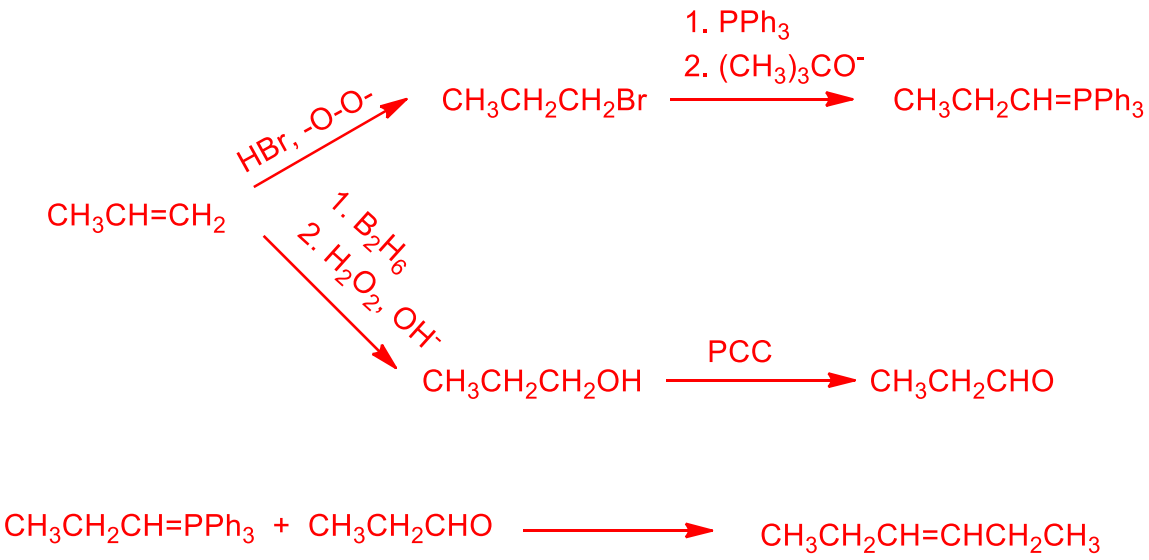
   a. *n*-butylbenzene



   b. 1-phenyl-2-propanone



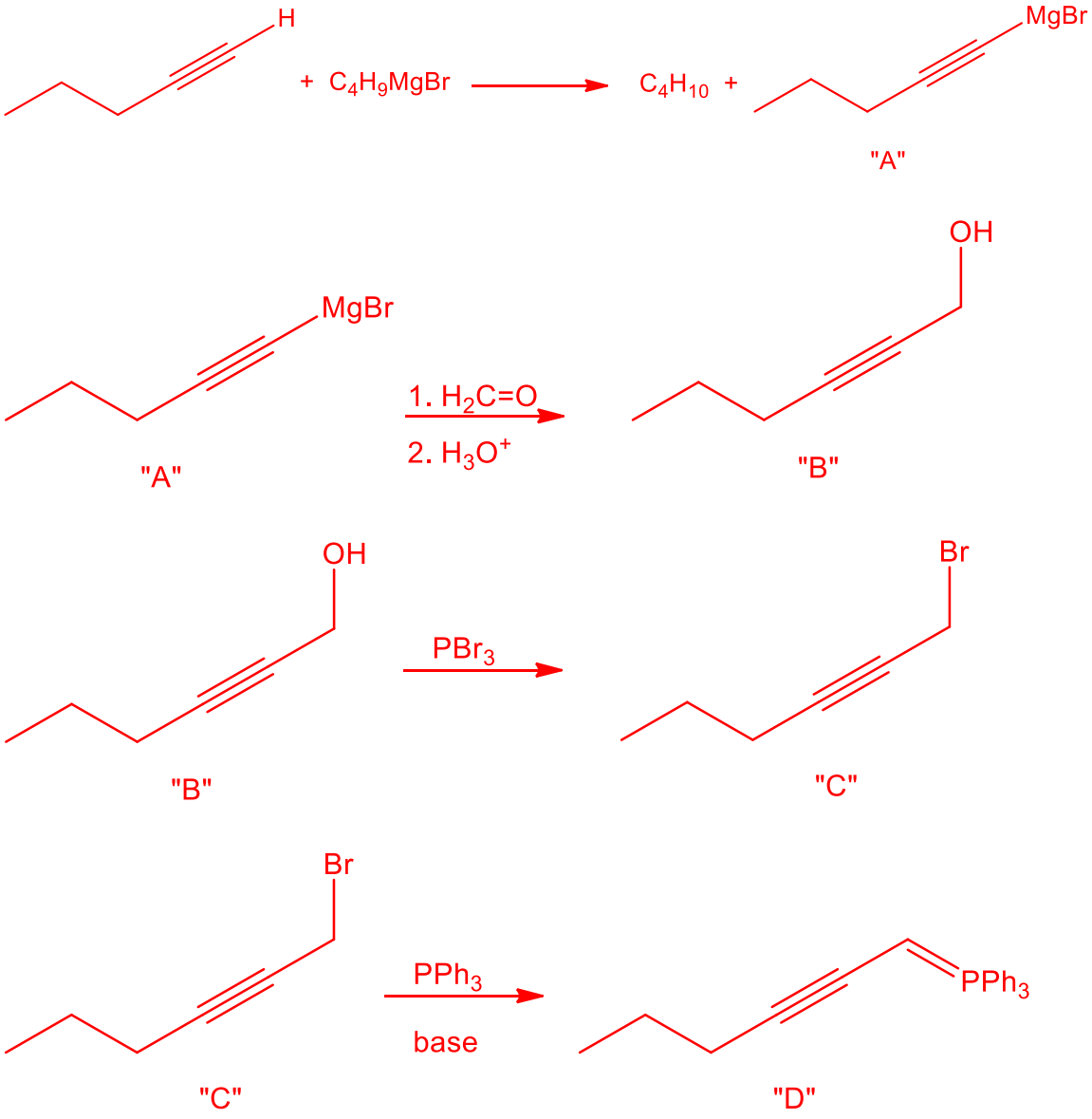
2. Outline a synthesis of 3-hexene from propene.

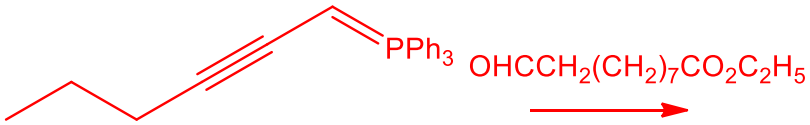


3. Bombykol, the sex pheromone of the silkworm moth, has been prepared in the following way:

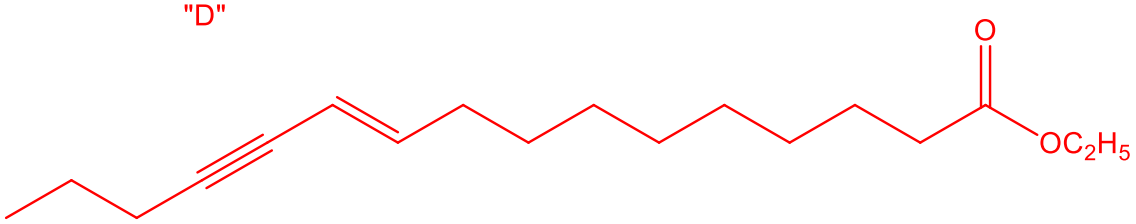
1-pentyne + n-C_4H_9MgBr → A (C_5H_7MgBr)
A + HCHO; then H^+ → B ($C_6H_{10}O$)
B + PBr_3 → C (C_6H_9Br)
C + Ph_3P, base → D ($C_{24}H_{23}P$)
D + $OHCCH_2(CH_2)_7CO_2C_2H_5$ → E ($C_{18}H_{30}O_2$)
E + H_2/Pd → F ($C_{18}H_{32}O_2$)
F + $LiAlH_4$ → bombykol ($C_{16}H_{30}O$)

Give the structures of compounds A to F and that of bombykol.



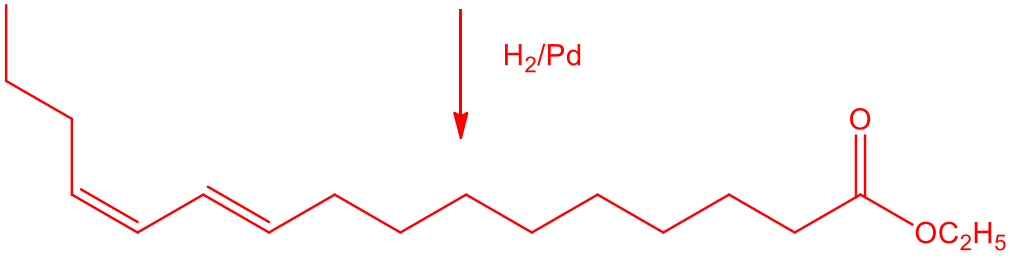


"D"



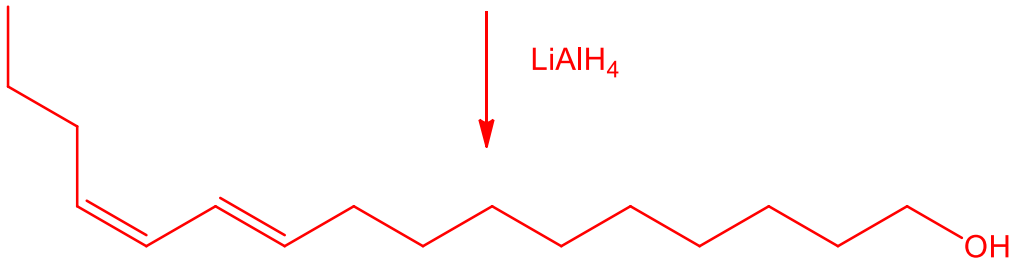
"E"

"E"



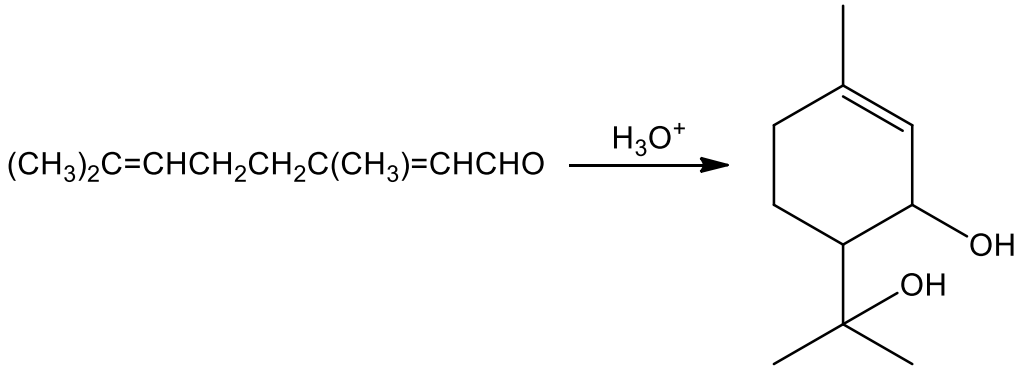
"F"

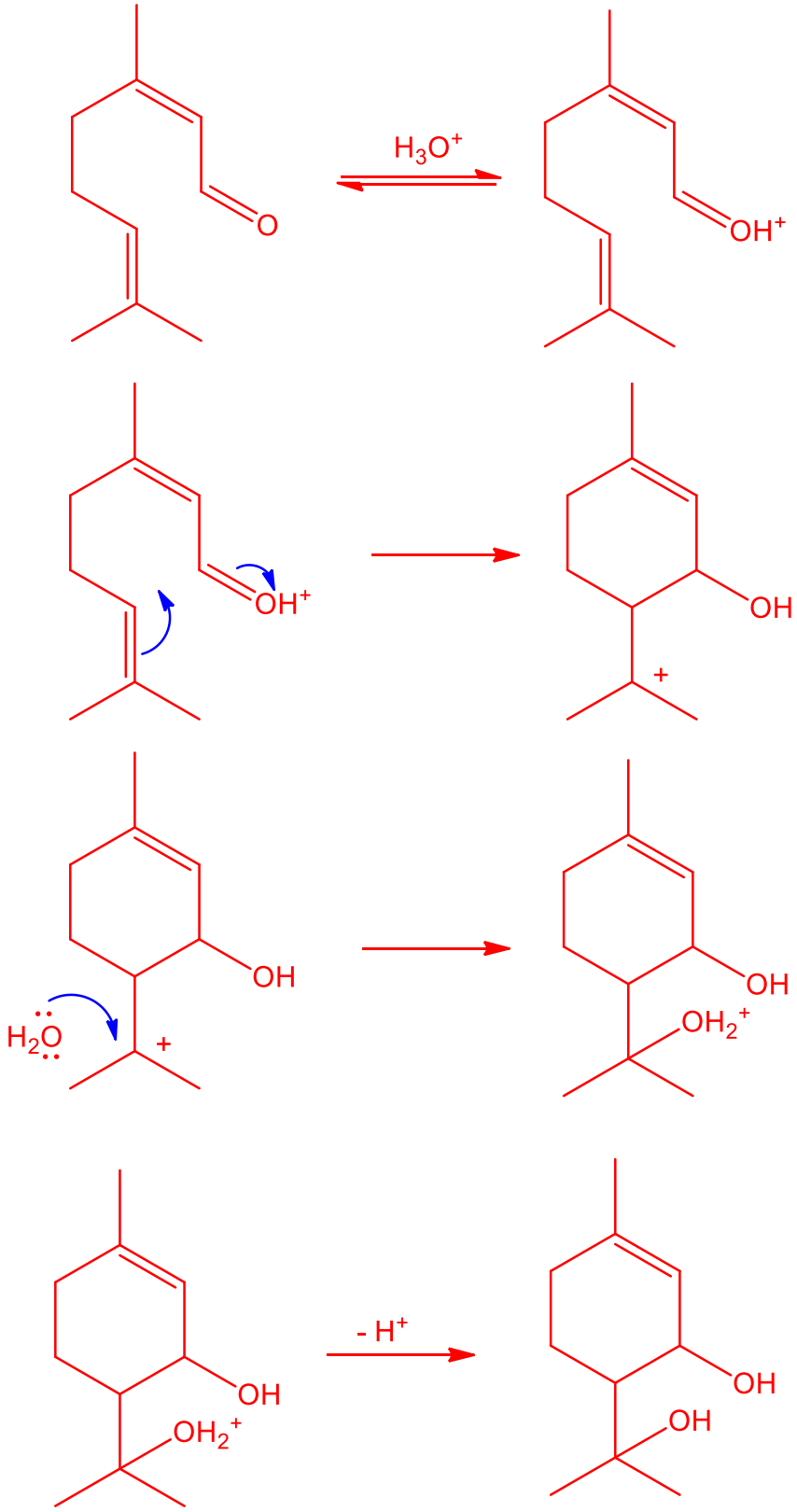
"F"



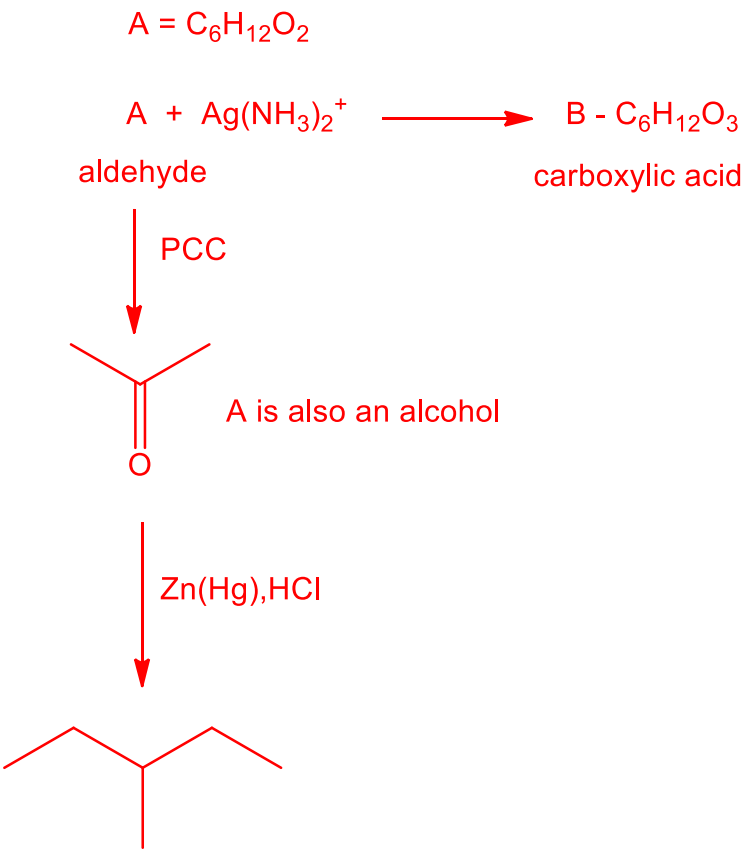
bombykol

4. Propose a mechanism for the following reaction:




H3O+
O
OH+
OH+
OH
+
H2O
OH
+
OH
OH2+
- H+
OH
OH2+
OH
OH

5. Compound “A”, $C_6H_{12}O_2$, was found to be optically active. Reaction with Tollens reagent gave “B”, $C_6H_{12}O_3$, an optically active carboxylic acid. Oxidation of “A” by pyridinium chlorochromate in dichloromethane gave an optically inactive compound which reacted with Zn(Hg)/HCl to give 3-methylpentane. Vigorous oxidation of “A” yielded “C”, $C_6H_{10}O_4$, an optically inactive dicarboxylic acid. Give the structures of compounds “A”, “B”, and “C”.



Vigorous oxidation of A gives a dicarboxylic acid therefore A is a primary alcohol. The diacid is optically inactive therefore the aldehyde and alcohol groups must be at the two ends of the chain. A is therefore: