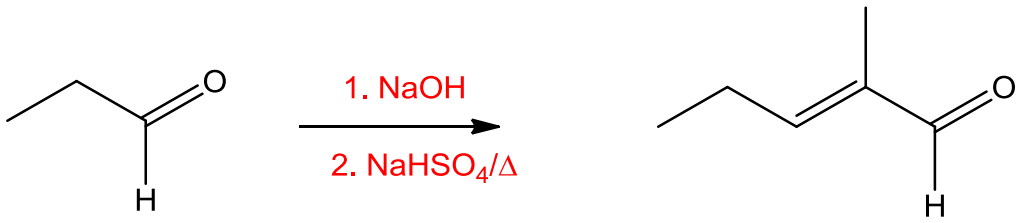
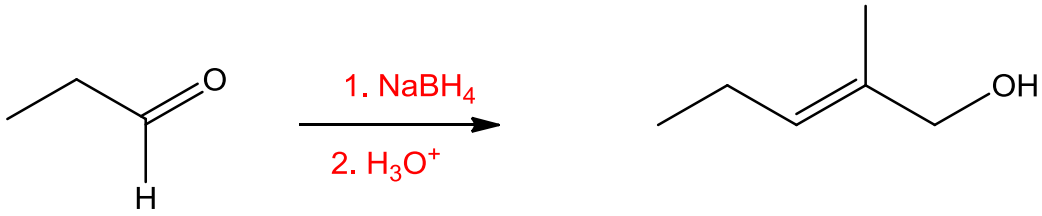
Problem Set 8 – Reactions of enolate ions

1. Write equations for the steps in each of the following syntheses:

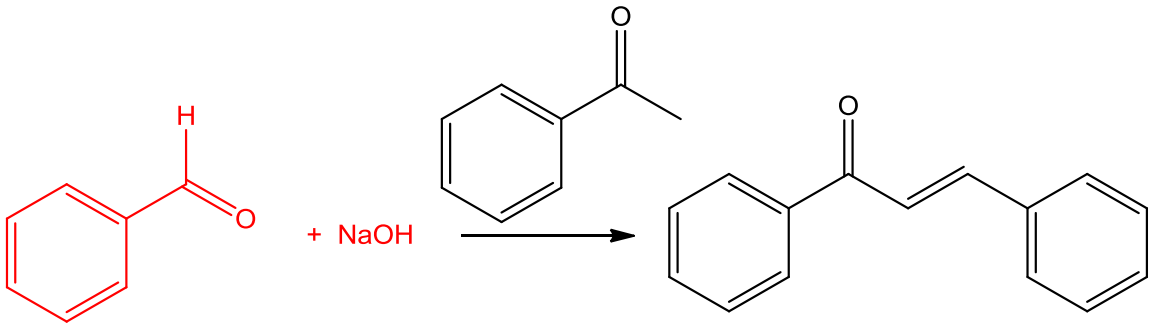
   a. propanal → 2-methyl-2-pentenal



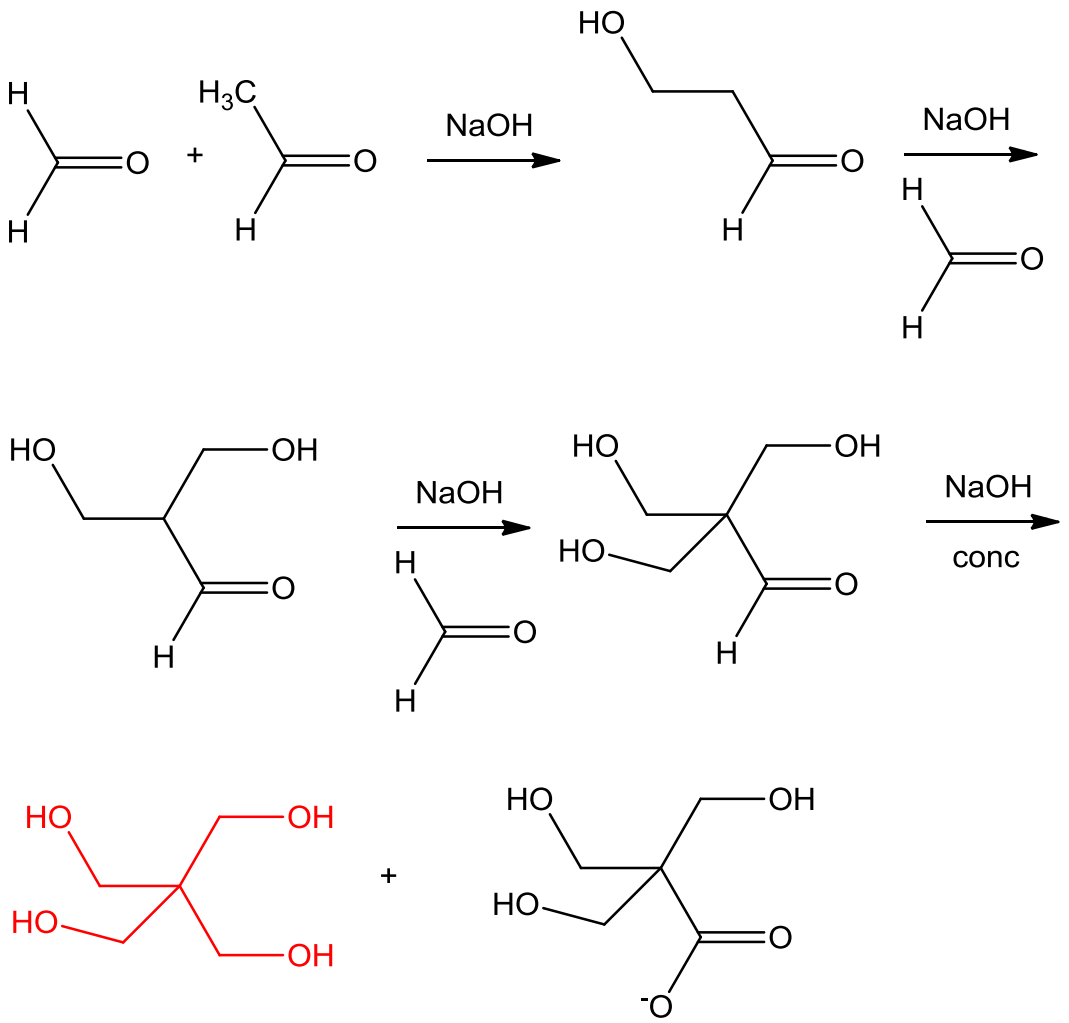
   b. propanal → 2-methyl-2-penten-1-ol



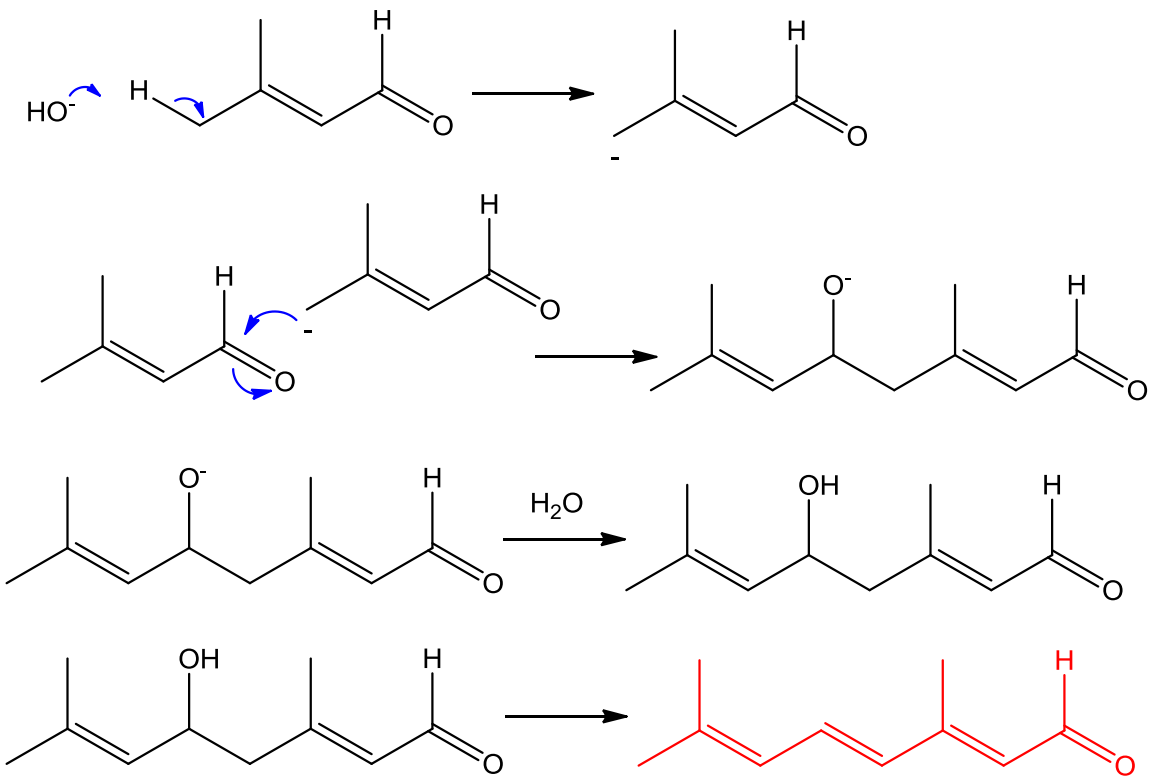
   c. acetophenone → 1,3-diphenyl-2-propen-1-one



2. Pentaerythritol, a compound used to make explosives, can be prepared by reacting acetaldehyde with formaldehyde in a basic solution. The reaction successively yields three compounds of formulae $C_3H_6O_2$, $C_4H_8O_3$, and $C_5H_{10}O_4$. Compound $C_5H_{10}O_4$, in the presence of concentrated NaOH, is converted into two compounds, pentaerythritol, $C_5H_{12}O_4$, and a sodium salt, $C_5H_9O_5Na$. What is the structure of pentaerythritol?

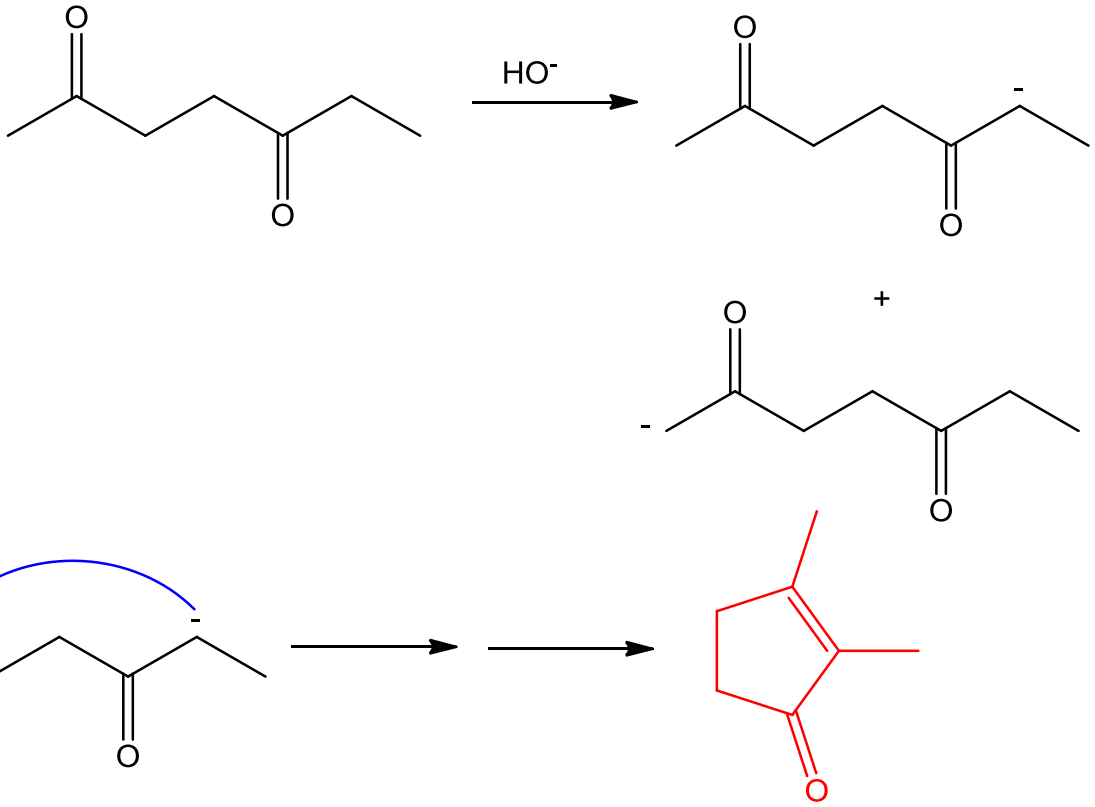


3. 3-methyl-2-butenal reacts with dilute NaOH to yield dehydrocitral, $C_{10}H_{14}O$. Deduce the structure of dehydrocitral.

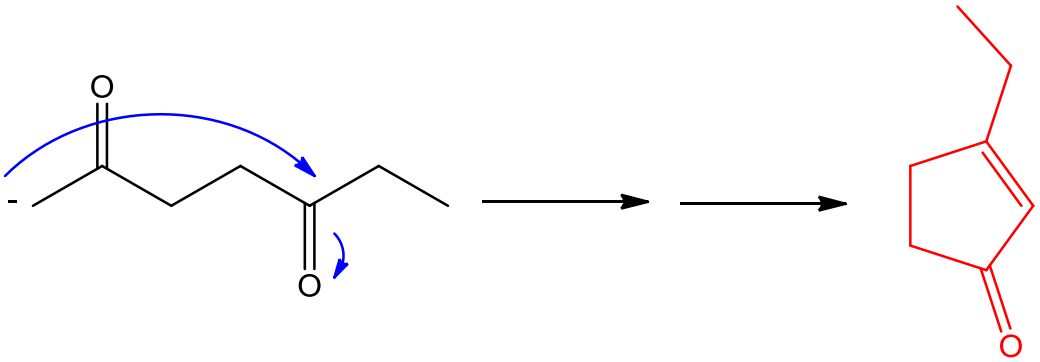


4. Intramolecular aldol cyclization of 2,5-heptanedione with dilute NaOH yields two enone products in the approximate ratio of 9:1. The major product has two singlet absorptions in its ^{1}H NMR spectrum at δ = 1.65 ppm and δ = 1.90 ppm. There are no absorptions in the range δ = 3 – 10 ppm.

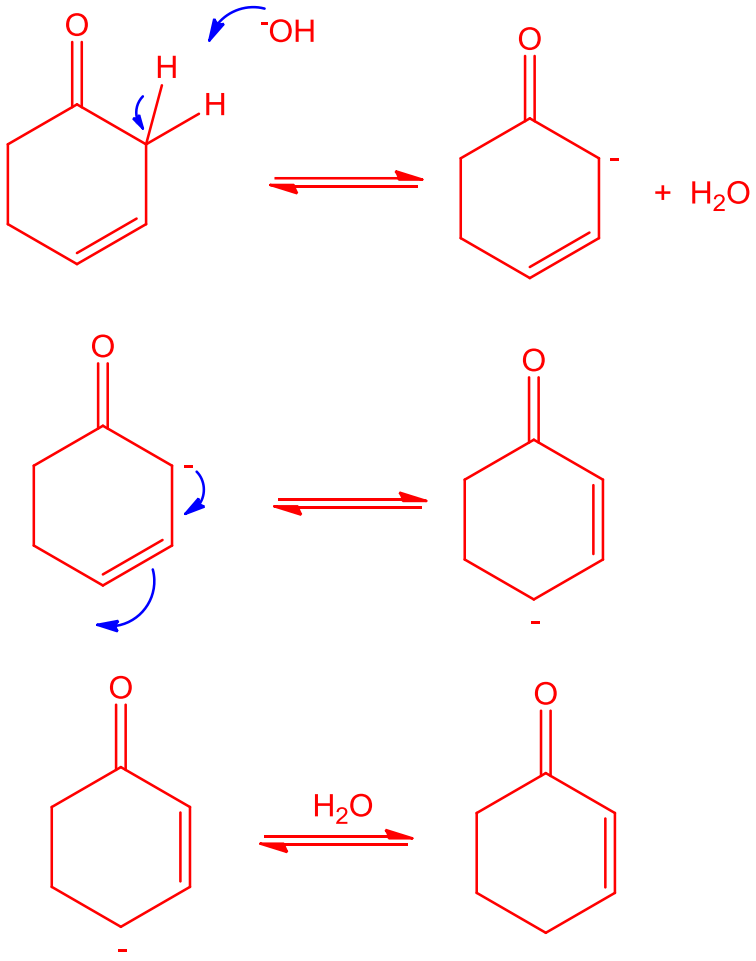
    a. What is the structure of the major product?



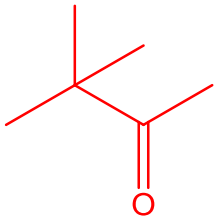
b. What is the structure of the minor product?



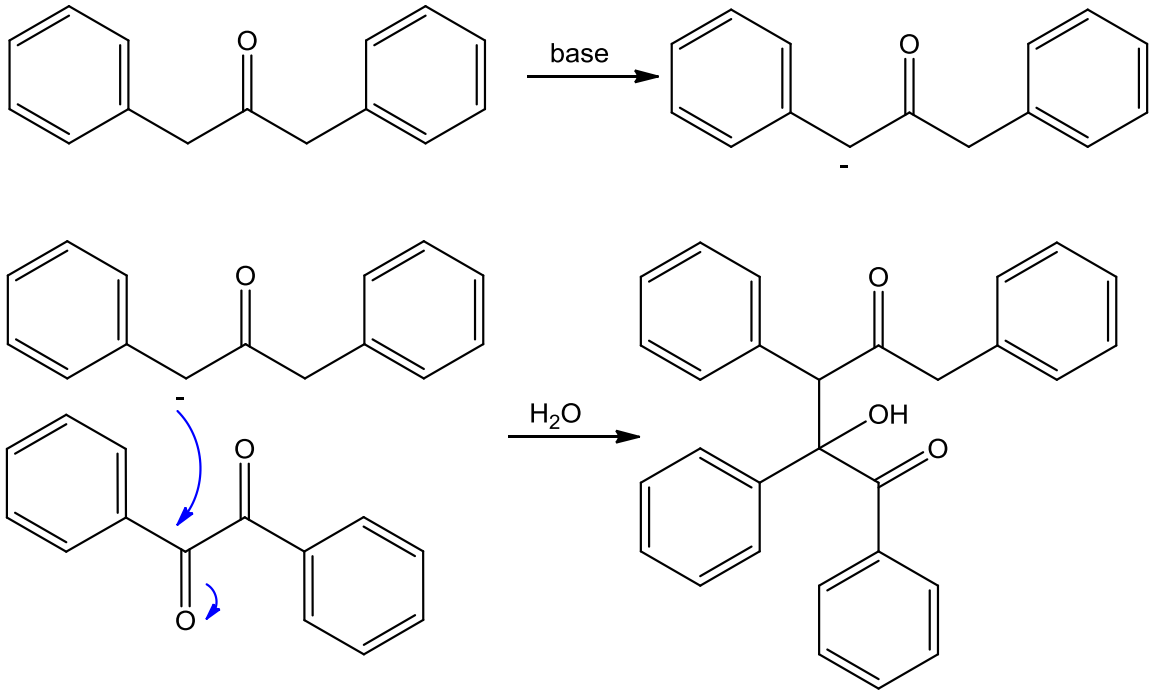
5. 3-cyclohexenone reacts with dilute NaOH to form an equilibrium mixture with 2-cyclohexenone. Propose a mechanism for this reaction.



6. Treatment of compound “A” with Br_2/NaOH followed by acidification gives bromoform and pivalic acid, $(CH_3)_3CCO_2H$. What is the structure of “A”?



7. 1,3-diphenyl-2-propanone, in the presence of alcoholic KOH, reacts with diphenylethanedione to yield a dark purple, cyclic ketone ($C_{29}H_{20}O$). What is the structure of this ketone.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base
O
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-
O
O
H2O
OH
O
O
OH
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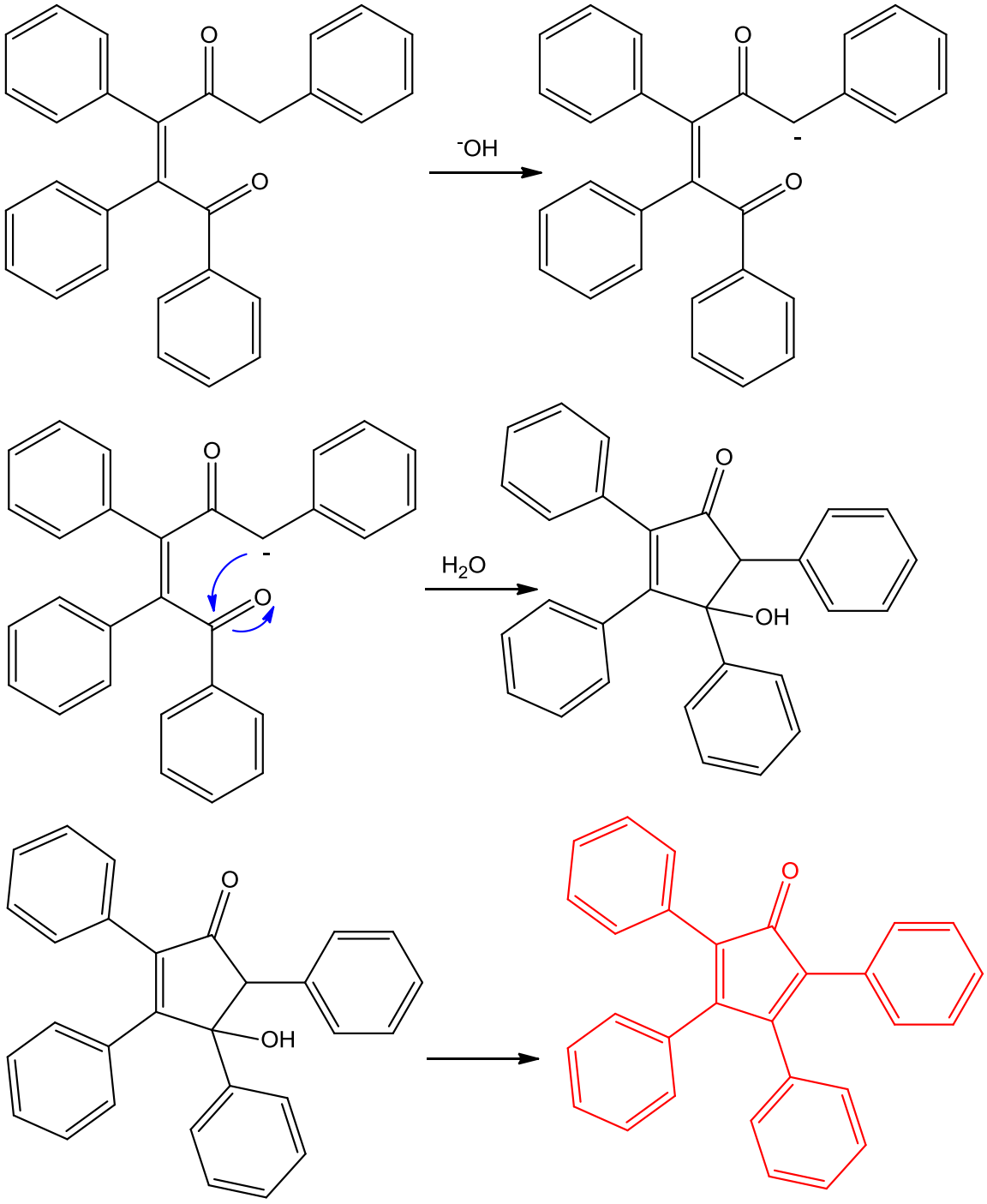
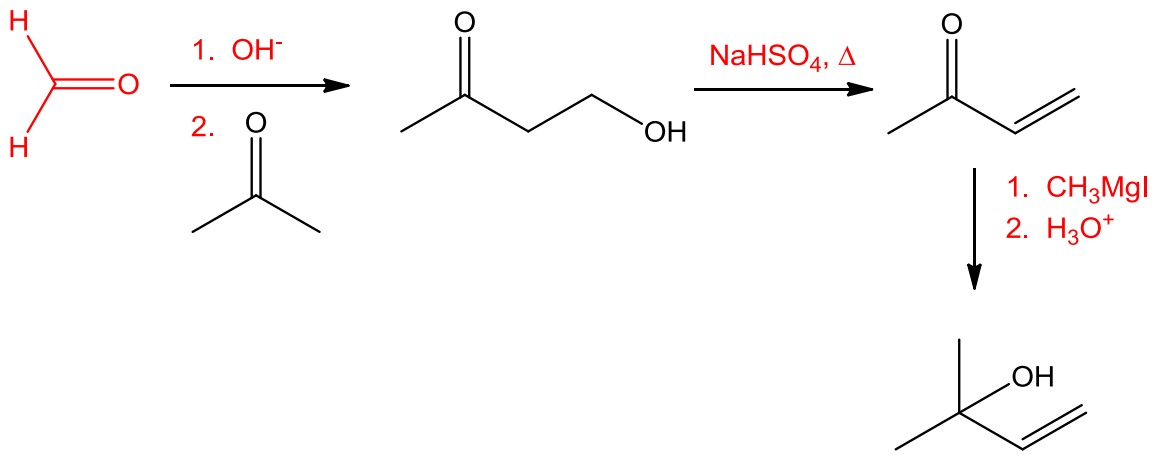
O



8. 2-methyl-3-buten-2-ol is one of the components of the sex pheromone of a destructive Scandinavian bark beetle. Propose a synthesis of this compound from acetone.


H
O
H
1. OH-
2.
O
O
OH
NaHSO4, Δ
O
1. CH3MgI
2. H3O+
OH