

Problem Set 8 – Reactions of enolate ions

- Write equations for the steps in each of the following syntheses:
 - propanal \rightarrow 2-methyl-2-pentenal
 - propanal \rightarrow 2-methyl-2-penten-1-ol
 - acetophenone \rightarrow 1,3-diphenyl-2-propen-1-one
- 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-methyl-2-butenal reacts with dilute NaOH to yield dehydrocitrinal, $C_{10}H_{14}O$. Deduce the structure of dehydrocitrinal.
- 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 1H NMR spectrum at $\delta = 1.65$ ppm and $\delta = 1.90$ ppm. There are no absorptions in the range $\delta = 3 - 10$ ppm.
 - What is the structure of the major product?
 - What is the structure of the minor product?
- 3-cyclohexenone reacts with dilute NaOH to form an equilibrium mixture with 2-cyclohexenone. Propose a mechanism for this reaction.
- 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"?
- 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.
- 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.