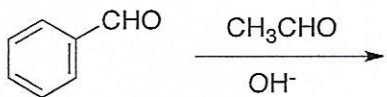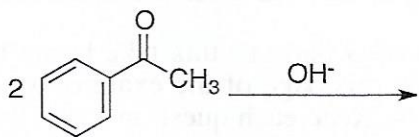## Part I. Predict the Product (50 pts)

A. Instructions: Give the expected <u>major</u> product or products in each of the following transformations. *Clearly show the stereochemistry where appropriate (i.e., with the use of wedged or dashed lines, or other unambiguous convention)*. Assume the appropriate standard work-up conditions (i.e., acid work-up or base work-up) that give the final neutral product. If no reaction is expected, write "NR".
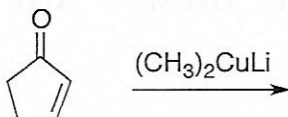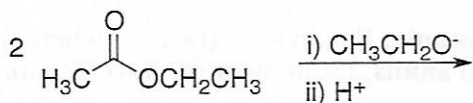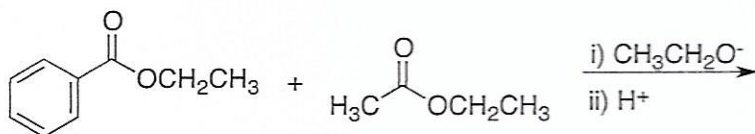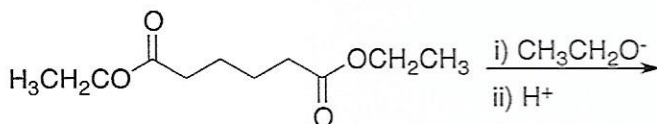
01.

02.

03.

04.

05.

06.

07.

08.

$$\text{PhCHO} + \text{H}_3\text{CH}_2\text{CO}_2\text{C}-\text{CH}_2-\text{CO}_2\text{CH}_2\text{CH}_3 \xrightarrow{\text{CH}_3\text{CH}_2\text{O}^-}$$

09.

$$\xrightarrow[\substack{\text{ROOR} \\ \text{(peroxides)} \\ \text{light}}]{\text{HBr}}$$

10.

$$\xrightarrow[\text{light}]{\text{Br}_2}$$
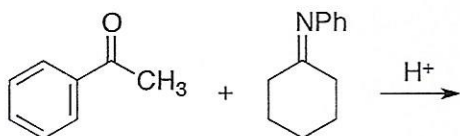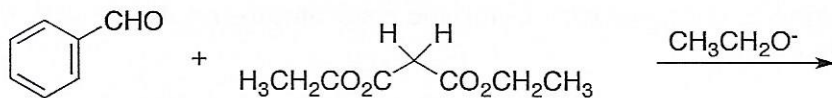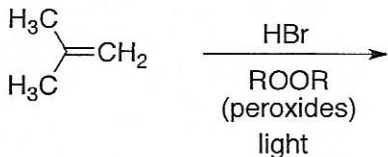
Part II. Mechanisms and Spectroscopy (50 pts)

A. When epoxy carboxylic acids are heated in the presence of pyridine, an aldehyde is formed via a rearrangement with the loss of CO_2. Using the electron-pushing formalism, show the mechanism for this transformation. (10 pts)
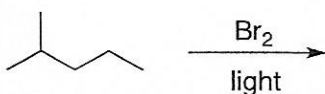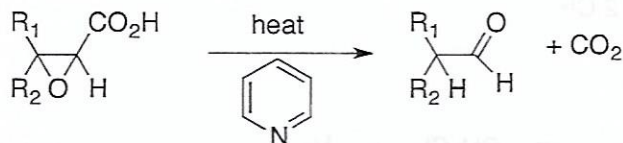

B. Treating a solution of *cis*-1-decalone with base causes an isomerization to take place. At equilibrium, the solution is found to contain about 95% *trans*-1-decalone and about 5% *cis*-1-decalone. Write a mechanism to account for this isomerization (05 pts). Why is the trans isomer favored? (05 pts).
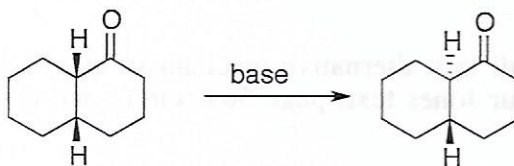
C. Aldehydes that have no α-hydrogens cannot undergo the aldol condensation. When these compounds are treated with base (e.g., hydroxide), they undergo instead an intermolecular oxidation-r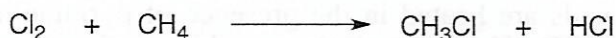eduction rection called the Cannizzaro reaction as shown below. Using the electron-pushing formalism, show the mechanism for this transformation. (10 pts)
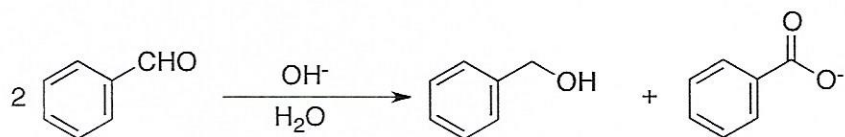
D. Shown below is an alternative mechanism for the photochemical chain radical chlorination of methane:

$$Cl_2 + CH_4 \longrightarrow CH_3Cl + HCl$$

Step 1 (initiation):

$$Cl_2 \longrightarrow 2 Cl\cdot$$

Step 2 (propagation, part 1):

$$Cl\cdot + CH_4 \longrightarrow CH_3Cl + H\cdot$$

Step 3 (propagation, part 2):

$$H\cdot + Cl_2 \longrightarrow HCl + Cl\cdot$$

1. Using the data provided below (bond dissociation energies, BDE), calculate $\Delta H°$ for each of the two propagation steps of the alternative mechanism (10 pts). BDE: C-H bond, 104 kcal/mol; C-Cl bond, 83 kcal/mol; Cl-Cl bond, 58 kca/mol; H-Cl bond, 103 kcal/mol.

$\Delta H°$ (step 2) = _____

$\Delta H°$ (step 3) = _____

2. Based on this information, will this alternative mechanism be: a) better; b) worse; or, c) about the same as the one discussed in your Jones text, page 569 (circle one choice, a, b, or c)? (05 pts) Justify your answer. (05 pts)

Part III. Synthesis (25 pts)

A. The structure of the analgesic Darvon is shown below. Starting with phenyl ethyl ketone, and using any reagents, reactions, or other materials we used in this course, devise a synthesis of Darvon. Partial syntheses will earn partial credit, so be sure to write any steps you know. (25 pts)