General Instructions:

(i) Use scratch paper at back of exam to work out answers; final answers must be recorded at the proper place on the exam itself for credit. Models are allowed.

(ii) Print your name on each page.

(iii) Please keep your paper covered and your eyes on your own work. Misconduct will lead to failure in the course.

1. (14 points) Show the major product(s) expected from the reactions below.

(a) \[
\text{H}_3\text{C} \quad \text{CH}_3 \quad \text{H}_3\text{C} \quad \text{CH}_3
\]

[Diagram showing chemical reaction]

(b) \[
\text{Br} \quad \text{H}_2\text{SO}_4 \quad \text{H}_2\text{O}
\]

[Diagram showing chemical reaction]
2. (24 points) Show the reagents required to convert the starting molecule to the indicated product. If necessary, be sure to differentiate clearly between distinct steps, by using "1)", "2)" etc. over the arrow.

(a) \[
\text{OH} \quad H\text{Cl}_2, \text{Et}_2\text{O} \quad \text{or} \quad \text{SOCl}_2 \quad \]

(b) \[
\text{OH} \quad \text{TsCl, pyridine or } \text{SOCl}_2 \text{ or } \text{PBr}_3 \quad \text{Na}_2\text{CN, DMSO} \quad \text{[or other leaving base]} \quad \]

(c) \[
\text{Cl} \quad \text{Mg}^2, \text{Li}^+ \quad \text{H}_2\text{O} \quad \text{K}_2\text{PO}_4 / \text{Li}^+ \quad \]

(d) \[
\text{Br} \quad (\text{C}_6\text{H}_{11}_2\text{CH}_2)_2\text{CuLi} \quad \text{or} \quad \text{Li}^+ \quad \text{Cu}^++ \quad \text{Br}^- \quad \text{or} \quad \]
3. (24 points) For each structure below, identify each chiral center with an arrow and indicate the configuration at that center.

Example: \[ R \rightarrow HO \quad H \]

For each pair, indicate the relationship between the pair, from four possibilities: constitutional isomers, diastereomers, enantiomers or identical. (Note that "conformational isomers" is not an option; such a relationship should be considered "identical.")

(a) \[ \text{R} \quad \text{S} \]
(b) \[ \text{R} \quad \text{S} \]
(c) \[ \text{R} \quad \text{S} \]
(d) \[ \text{R} \quad \text{S} \]

Constitutional Isomers Enantiomers Diastereomers

\[ \text{Identical} \]

+1 for each correct R/S
+2 for each correct circle
4. (12 points) Of the two reactions shown below, #2 is faster. Explain this observation, using an energy diagram (showing both reactions) to illustrate your argument.

This energy difference determines relative rates, because first step is rate-determining step.

Allylic cation is more stable than 2° cation intermediate (resonance stabilization in former). This energy difference should be reflected in the relative energies of the transition states for carbocation formation (Hammond postulate).

Correct energy diagrams (2 steps; first is RDS)

= +3 for each react.
5. (16 points) Explain why treating the alkyl bromide shown below with tBuONa alone does not lead to a reaction, and show a mechanism for the reaction that occurs with tBuONa plus NaI.

Starting material =

Neither chair conformation has an H anti-polar plane to the Br. Therefore, $S_2$ mechanism impossible. Since the reagents and conditions don't favor $E1$, $S_N 2$ or $S_N 1$, there is no rxn in any case. For bottom:

- $+1$ for arrows
- $+1$ for arrows
- $+2$ for arrows
- $+1$ for arrows
6. (10 points) Of the two reactions shown below, the upper is one we have discussed in class (bromohydrin formation). Provide a mechanism for the lower reaction, which occurs when base is included in the reaction mixture.

\[ \text{Br}_2 \xrightarrow{\text{H}_2\text{O}} \text{OH-Br} \] 

\[ \text{Br}_2 \xrightarrow{\text{NaOH, H}_2\text{O}} \text{Br} \]