Detailed Mechanism Provide a detailed mechanism [i.e., explicitly show (using curly arrows) EVERY intermediate, formal charge (where relevant), equilibrium, and bond-making and -breaking step] to account for the following transformations:

a) The conversion of the substituted diene 1 to its rearranged analogue 2. Provide a 3D drawing of the transition state that accounts for the formation of the (E)-alkene.

b) Formation of a cyclic enone 4 from cyclic enol silane 3. [Hint: Molecular oxygen oxidizes Pd(0) to Pd(II) in this catalytic system.]

c) The thiamine-based benzoin condensation is considered a “green” alternative to using cyanide reagents. Provide a detailed mechanism to account for the formation of benzoin 6 from substituted benzaldehyde 5.
Other Problems

1. When the stannane $Z$-7 was exposed to $n$-butyllithium and then quenched with acid, the homoallylic alcohol 8 was formed in a highly diastereoselective process (i.e., to give the $E,S$ stereoisomer 8). However, when $E$-7 was exposed to the same conditions, a nearly 1:1 ratio of diastereomers ($E,S$ and $E,R$) was formed. Rationalize this result using an A$^{1,3}$-strain argument, accompanied by drawings.

2. Upon exposure of the $\gamma$-hydroxymesylate 9 to sodium acetate in hot aqueous acetic acid, a highly polar medium, the tetrahydrofuran 10 was formed. Rationalize the observed stereochemical outcome of this transformation.

3. During the oxidation of 1-decanol 11 using the Corey-Kim reagent (from NCS and DMS) at -25 °C for 1.5 hours, 1-decanal 12, recovered 11, and the undesired byproduct thiomethyl ether 13 were produced. If the Swern oxidation (CICOCOCl and DMSO) is used instead, the formation of 13 is greatly reduced. Propose a mechanism for the formation of the byproduct 13 and rationalize why the Swern oxidation gives superior results.

4. Reaxys Database Search

a. According to the Reaxys database, how many single-step transformations convert any $\beta$-carbonyl-containing ketone to a pyrimidine using any amidine?

b. According to the Reaxys database, how many single-step transformations convert a $\beta$-ketoester (what does $R^1$ need to be?) to a pyrimidine using any amidine?

c. According to the Reaxys database, how many single-step transformations convert any $\beta$-carbonyl-containing ketone to a pyrimidine containing a heteroaromatic substituent at its 2-position (what does $R^2$ need to be)?