Friday Problem Set
January 15, 2010
Presented by Christopher D. Thomas

Tandem Use of Cobalt-Mediated Reactions to Synthesize (+)-Epoxycymene, a Diterpene Containing a Trans-Fused 5-5 Ring System

1. Please give a mechanism for the following reaction, along with the name of the reaction. (Tetrahedron 1965, 21, 1247.)

\[
\text{Me} \quad \text{Me} \\
\text{O} \quad \text{Me} \\
(\text{R})-\text{pulegone}
\]

\[
\begin{align*}
1) \text{Br}_2 \\
2) \text{NaOMe, MeOH}
\end{align*}
\]

\[
\text{Me} \quad \text{Me} \\
\text{Me} \quad \text{CO}_2\text{Me}
\]

2. Please give a mechanism for the following reaction, along with the name of the reactions involved in the process. (J. Am. Chem. Soc. 1986, 108, 3128.)

\[
\begin{align*}
\text{Co(CO)}_3 & \quad \text{Co} \\
\text{Me} & \quad \text{Me} \\
\text{TMS} & \quad \text{H} \\
\text{Et}_2\text{AlCl, CH}_2\text{Cl}_2 & \quad \text{-78 \text{°C}, 83% yield} \\
& >20:1 \text{ d.r.}
\end{align*}
\]

3. Rationalize the following questions about 5,5 and 6,6 bicycles:

a) Why is the cis-fused bicyclo[3.3.0]octane more stable than the trans-fused?

\[
\begin{align*}
\Delta G &= +6.4 \text{ kcal/mol}
\end{align*}
\]

b) In the 1,4-reduction of an octalone system, why is the trans-product favored? Please draw a transition state with molecular orbitals to illustrate.

[Diagram showing transition state]