CEM 351
3rd EXAM/Version A
Friday, November 21, 2003
1:50 – 2:40 p.m.
Room 138, Chemistry

Name (print) ____________________________
Signature ______________________________
Student # _______________________________
Section Number __________________________

Grade?
☐ □ 1.(20 pts.)__________
☐ □ 2.(20 pts.)__________
☐ □ 3.(20 pts.)__________
☐ □ 4.(20 pts.)__________
☐ □ 5.(20 pts.)__________
☐ □ 6.(20 pts.)__________

TOTAL 100 pts.)

Score

Note: Answer any 5 questions for a total score of 100 pts. Be sure to look over all the questions first before beginning the exam, and indicate which five questions are to be graded by checking the corresponding box.
1. (4 pts each; 20 total) Draw 3D representations of the products expected from the following Diels-Alder reactions in the boxes provided. Don’t forget about the endo preference:

(a) ![3D representation of the product](image)

(b) ![3D representation of the product](image)

(c) ![3D representation of the product](image)

(d) ![3D representation of the product](image)

(e) Recalling that “t-Bu” stands for the tertiary butyl group, -C(CH\(_3\))\(_3\), explain why the reaction shown in (c) is fine, but the one in (d) would, in fact, almost certainly not react, although it is easy to draw a picture of the intended product.

The two t-Butyl groups suffer extreme steric repulsion when they are in a cis relationship, so that the diene would never achieve the necessary conformation to be able to undergo the Diels-Alder reaction.
2. (20 pts) Addition of Br₂ to double bonds under nonradical conditions usually occurs with specific stereochemistry. For instance, though both cis- and trans-2-butene react with bromine to form optically inactive products, one forms a meso compound, and one forms a racemic mixture. Racemic and meso bromonium ion intermediates also play a role. Here we consider these reactions. Draw the intermediates and products for the two Br₂ additions shown below (2 pts each; 6 structures total) first; then circle the appropriate (“meso” or “racemic”) labels for each box (2 pts each; 4 labels). Remember: for the racemic species be sure to draw both enantiomers.

(a) 

\[ \text{Diagram:} \quad \text{Bromonium bromides} \quad \text{Dibromide products} \]

\[ \text{B} \text{r}^+ \quad \text{B} \text{r}^- \quad \text{B} \text{r}^- \quad \text{B} \text{r}^+ \]

\[ \text{meso} \quad \text{racemic} \quad \text{meso} \quad \text{racemic} \]

(b) 

\[ \text{Diagram:} \quad \text{Bromonium bromides} \quad \text{Dibromide products} \]

\[ \text{B} \text{r}^+ \quad \text{B} \text{r}^- \quad \text{B} \text{r}^- \quad \text{B} \text{r}^+ \]

\[ \text{meso} \quad \text{racemic} \quad \text{meso} \quad \text{racemic} \]
3. (a) (9 pts) Write expressions for the equilibrium constants for the following reactions:

i) \[ \text{H}_2\text{C} = \text{CH}_2 + \text{Br}_2 \rightleftharpoons \text{Br–CH}_2\text{–CH}_2\text{–Br} \]
\[ K_{eq} = \frac{[\text{Br–CH}_2\text{–CH}_2\text{–Br}]}{[\text{H}_2\text{C} = \text{CH}_2][\text{Br}_2]} \]

ii) \[ (\text{CH}_3)_3\text{C} – \text{OH} + \text{H}_3\text{O}^+ + \text{Cl}^- \rightleftharpoons (\text{CH}_3)_3\text{C} – \text{OH}^+ + \text{H}_2\text{O} + \text{Cl}^- \]
\[ K_{eq} = \frac{[(\text{CH}_3)_3\text{C} – \text{OH}^+][\text{H}_2\text{O}]}{[(\text{CH}_3)_3\text{C} – \text{OH}][\text{H}_3\text{O}^+]} \]

Note: \( \text{Cl}^- \) on both sides cancels and contributes nothing to \( K \) value.

iii) \[ (\text{CH}_3)_3\text{C} – \text{I} + \text{HI} \rightleftharpoons (\text{CH}_3)_3\text{C} – \text{H} + \text{I}_2 \]
\[ K_{eq} = \frac{[(\text{CH}_3)_3\text{C} – \text{H}][\text{I}_2]}{[(\text{CH}_3)_3\text{C} – \text{I}][\text{HI}]} \]

(b) (5 pts) Using the following bond strength data (in kcal/mol), calculate the \( \Delta H_{\text{rxn}} \) for reaction (iii) in part (a) above:
\( \text{(CH}_3)_3\text{C} – \text{H} = 95.2; (\text{CH}_3)_3\text{C} – \text{I} = 53.7; \text{H–I} = 71.3; \text{I–I} = 36.1 \)
Then, for 25°C, and assuming \( \Delta S = 0 \) so that \( \Delta G_{\text{rxn}} = \Delta H_{\text{rxn}} \), calculate the value of \( K_{\text{rxn}} \).
If you don’t have a calculator, just set up the expression. Remember, \( R = 1.987 \) cal/mol K.

Break C–I, H–I bonds; 53.7 + 71.3 = 125.0 kcal/mol
Make C–H, I–I bonds; –95.2 –36.1 = −131.3 kcal/mol
So \( \Delta H_{\text{rxn}} = 125.0 - 131.3 = -6.3 \) kcal/mol = -2.3 x \( R \times T \times \log K \)
So \( K = 10^{-0.3(25°C - 298) / 1.987} = 10^{-4.6} = 4.2 \times 10^4 \)
i.e. reaction is downhill and \( K > 1 \)

(c) (6 pts) Draw a mechanism (6 steps) for the sodium amide-catalyzed isomerization of 2-butyne to 1-butyne.

Exothermic, irreversible steps; Remember, sp hybridized carbon is lower in \( E \) than isomeric anions.
4. (20 pts) Quick true/false statements; please circle your answers (4 pts each):

(a) Between the kinetic and the thermodynamic products of a reaction, the kinetic product is formed faster and the thermodynamic product is the more stable.

True  False

(b) If one reaction is more exothermic than another, it is always the faster reaction.

True  False

(c) Aromatic compounds are always six-membered rings like benzene.

True  False

(d) Diels-Alder dienophiles are often alkenes that are substituted with electron-withdrawing groups.

True  False

(e) Because the chlorine-carbon bond is so strong, radical addition of H-Cl to alkenes occurs readily.

True  False

5. (20 pts) Quick chemical answers (4 pts each):

(a) Circle the epoxidizing agent:

\( t\text{-BuO-Ot-Bu} \)  \( \text{CH}_3\text{C} (=\text{O})\text{OOH} \)

(b) Circle the compound with the strongest bond to H:

\( \text{HO–H} \)  \( \text{CH}_3–\text{H} \)

(c) Circle the aromatic compound:

(d) Circle the conjugated diene:

(e) Circle the less stable \( \text{C}_6\text{H}_{11} \) radical:
6. (8 pts) (a) As we mentioned in class, Vitamin E is a powerful antioxidant capable of capturing free radicals that cause cellular damage in living organisms. The synthetic antioxidant BHT, commonly found in packaged foods, performs a similar function, preventing development of rancidity. Assuming that the free radical species \( \text{R}^+ \) would initially abstract a hydrogen atom from the OH functionalities of these compounds, use the BHT framework to draw the four resonance forms that would rationalize the stability of the resulting phenoxy radicals.

\[
\begin{align*}
\text{Vitamin E} & \quad \text{BHT} \\
\end{align*}
\]

(b) (6 points) Speaking of rancidity, why are the most easily abstracted H atoms (i.e. weakest C-H bond strengths) in natural oils (e.g. vegetable oils) the ones that lie between two double bonds? Provide an explanation in terms of the free radical product of C-H bond breaking.

\[
\begin{align*}
\text{Most reactive H's} \\
\text{A generic diunsaturated vegetable oil} \\
\end{align*}
\]

(c) (6 pts) We think of the allyl radical (\( \text{H}_2\text{C} = \text{CH}-\text{CH}_2^+ \)) as being stabilized by delocalization. But the half-filled nonbonding orbital in allyl lies at the same energy level as a localized nonbonding p orbital. Consider the diagram below, showing a radical p orbital interacting with a double bond in an end-on manner. Draw the top and bottom energy levels and electrons and the three orbitals that result from this interaction, and explain what leads to the overall stabilization when these fragments get together (Hint—focus on bonding and antibonding orbitals too).

\[
\begin{align*}
\text{Localized radical in p orbital} \\
\text{ Allyl radical} \\
\text{Double bond} \\
\text{Radical formation between the two bonds allows both to stabilize the radical by allylic resonance--i.e. delocalization.} \\
\end{align*}
\]

The energy of the \( \pi \)-bonding electron pair is lowered when it is extended to three orbitals with all bonding interactions, so the overall system's energy is lowered, but it's this stabilization of the bonding orbital rather than of the orbital containing the single electron itself that is responsible.