I (22 points) Diels-Alder reaction from Resonance Structure to regio- and stereochemistry

a) Which of the following resonance structures of acetone is more stable (A or B)?

\[
\begin{align*}
\text{A} & \quad \text{B} \\
\end{align*}
\]

b) Which atom (C or O) in acetone do you think is more likely to be attacked by a nucleophilic anion?

\[
\begin{align*}
\text{HO-} & \quad \text{C} \\
\end{align*}
\]

c) Which of the following resonance structures of methylvinylketone is more stable (A or B)?

\[
\begin{align*}
\text{A} & \quad \text{B} \\
\end{align*}
\]

d) Which carbon (α or β) in methylvinylketone do you think is more likely to be attacked by a nucleophilic anion?

\[
\begin{align*}
\text{HO-} & \quad \alpha \quad \beta \\
\end{align*}
\]

e) Which of the following resonance structures of 1-methoxybutadiene is more stable (A or B)?

\[
\begin{align*}
\text{A} & \quad \text{B} \\
\end{align*}
\]

f) Which atom (C-1 or C-4) in 1-methoxybutadiene do you think is more likely to be protonated?
g) Which of the following regioisomeric Diels-Alder products is more likely to form (A or B)?

![Diels-Alder reaction diagram with options A and B]

h) Which of the following regioisomeric Diels-Alder products is more likely to form (A or B)?

![Diels-Alder reaction diagram with options A and B]

i) Which of the following diastereomeric Diels-Alder products is more likely to form (A or B)?

![Diels-Alder reaction diagram with options A and B]

j) In which of the following Diels-Alder products (A or B) is the electron-withdrawing group closer to the remaining alkene?

![Diels-Alder reaction diagram with options A and B]

k) In which of the following Diels-Alder products (A or B) is the electron-withdrawing group closer to the remaining alkene?

![Diels-Alder reaction diagram with options A and B]
When 2-methyl-1,3-cyclopentadiene 1 is mixed with methyl 2-methylacrylate 2 a Diels-Alder cycloaddition reaction occurs to give a mixture of two racemic products with the endo product being major and the exo product being the minor product formed (see reaction below). Please answer the following questions about this [4+2]-cycloaddition reaction. (2 points each)

![Diagram of Diels-Alder reaction]

a) In the box below please indicate, which of the above products (A, B, C, or D) is the most likely endo product?

![Box for selecting endo product]

b) In the box below please indicate, which of the above products (A, B, C, or D) is the most likely exo product?

![Box for selecting exo product]

c) If the 2-methyl-1,3-cyclopentadiene 1 was changed to 2-methyloxy-1,3-cyclopentadiene 3 would you think the resulting Diels-Alder reaction to occur at a faster, slower or the same rate? Please indicate, by circling the answer below.

![Diagram of 2-methyloxy-1,3-cyclopentadiene 3]

Faster  Slower  Same

![Box for selecting rate of reaction]

d) If the 2-methyl-1,3-cyclopentadiene 1 was changed to 2-methyl-1,3-butadiene 4 would you think the resulting Diels-Alder reaction to occur at a faster, slower or the same rate? Please indicate, by circling the answer below.

![Diagram of 2-methyl-1,3-butadiene 4]

Faster  Slower  Same

![Box for selecting rate of reaction]
e) If the 2-methyl-1,3-cyclopentadiene 1 was changed to 1-methyl-Z-1,3-butadiene 5 would you think the resulting Diels-Alder reaction to occur at a faster, slower or the same rate? Please indicate, by circling the answer below.

5

Faster  Slower  Same

f) In the space provided below please draw the major product of the Diels-Alder reaction between 2-ethoxy-1,3-butadiene and acrylaldehyde (aka, prop-2-enal). If the product is chiral or achiral, please indicate so. In addition if the product has more than one chiral center, please indicate if it is the RR/SS or the RS/SR product. (5 points)

i)  

ii) Chiral or Achiral

iii) (R,R,S,S) or (R,S,S,R)

(3 points)

g) In the space provided below please draw the major product of the Diels-Alder reaction between 1-ethoxy-1,3-butadiene and acrylaldehyde (aka, prop-2-enal). If the product is chiral or achiral, please indicate so. In addition if the product has more than one chiral center, please indicate if it is the RR/SS or the RS/SR product. (5 points)

i)  

ii) Chiral or Achiral

iii) (R,R,S,S) or (R,S,S,R)

(3 points)