Practice Problems on Diels-Alder Reactions – Answers

1. Predict the product of the following Diels-Alder reactions; under kinetic control. Include the stereochemistry where appropriate.

(a) ![Furan + Maleic acid](image)

(b) ![Maleimide + Vinylaldehyde](image)

(c) ![Naphthalene + Acrylic acid](image)

(d) ![Maleic anhydride + Maleic acid](image)

2. Furan and maleimide, shown below, react to produce and adduct via a Diels-Alder reaction. At 25°C the isomer produced is the endo product, however at 90°C the exo isomer predominates. Additional studies have shown that at 90°C the equilibrium between the endo and exo products favors the exo isomer.

(a) Draw each isomeric product, endo and exo.

![endo isomer](image)  ![exo isomer](image)

(b) Which isomer would you expect to usually form in this reaction? Why is that isomer usually preferred?

The endo product is the preferred outcome of the Diels-Alder reaction under kinetic control. The transition state to the endo product has lower activation energy than transition state of the exo product.

(c) Is your answer to question 4(b) dependent on a kinetically or thermodynamically controlled reaction?

Yes. Each of the conditions is dependent on different aspects of a chemical reaction. While in kinetically controlled conditions the products formed depend on the difference in activation energy; thermodynamic conditions depend on the energy difference of the products.
d) Explain why the *endo* isomer predominates when the reaction takes place at 25°C and why the *exo* isomer at 90°C.

The reaction at 25°C is under kinetic control, therefore the product whose transition state activation energy is lower will be the predominant which in this case is the *endo* product.

3. When 1,3-butadiene reacts with compound D two products are formed. Draw the structures of each.

\[
\text{H}_{2}C\text{CH} = \text{CHCH} \text{COO} \text{H} + \text{HOOC}\text{CH} = \text{COO} \text{H} \rightarrow
\begin{align*}
\text{CH}_{3}\text{CH} = \text{CHCH} \text{COO} \text{H} &\quad \text{CH}_{3}\text{CH} = \text{CHCH} \text{COO} \text{H} \\
\end{align*}
\]

4. Compound A, C₄H₆, reacts with one of the diastereomers, B, of CH₃O₂CCH=CHCO₂CH₃ to form 2 enantiomeric products, C & D. On the other hand when B’ (the other diastereomer) reacts with A only one product is formed, E. Determine the identity of compounds A through E.

\[
\begin{align*}
\text{CH} = \text{CHCH} \text{COO} &\quad \text{CH} = \text{CHCH} \text{COO} \\
\text{CH} = \text{CHCH} \text{COO} &\quad \text{CH} = \text{CHCH} \text{COO} \\
\text{CH} = \text{CHCH} \text{COO} &\quad \text{CH} = \text{CHCH} \text{COO} \\
\end{align*}
\]

5. Which diene and dienophile could be used in the synthesis of each of the following.