This assignment looks at two issues:
- Orbital vs. charge-control of enolate chemistry
- Frontier MO interactions and transition state properties

Orbital vs. charge-control of enolate chemistry

Do the following problems in Chapter 11 (Enolates as Nucleophiles) in the Molecular Modeling Workbook:
- Problem 8: Enolates are Ambident Nucleophiles
- Problem 9: Silylation of Enolates

Note: the models for these problems are located on the CD.

Frontier MO interactions and transition state properties

I’m providing you with models that will allow you to analyze the following cycloaddition reactions in detail.

Both reactions involve diazomethane, CH$_2$N$_2$, and the obvious issue for each reaction is regioselectivity. Fleming says that both reactions yield the same regioisomer, the left-hand product, which raises a second question. If electron-rich and electron-poor alkenes yield the same regioisomer, do the reactions follow the same reaction mechanism and share the same transition state?

I’d like you to analyze these two questions, regioselectivity within a given reaction and similarities between reactions, from several points of view, and write a short paper describing your analysis. Here are some ideas to guide you:

1. Use models of the reactants and frontier MO theory to predict regioselectivity for each reaction. A couple of questions to consider: Is there a dominant frontier orbital interaction in each reaction? (If there is, what is it?) What is the favored
regioisomer? What do the frontier orbital interactions imply about the direction and extent of electron flow in the transition state? What do these interactions imply about transition state geometry? Make sure you explain your reasoning. Don’t just make statements like “regioisomer A is preferred”.

2. Use models of the four transition states to predict regioselectivity for each reaction. A couple of questions to consider: What product ratio is predicted at room temperature? Are the two reactions predicted to be equally selective? Do these models support your frontier MO analysis?

3. Try to integrate the properties of the transition state models with the predictions made by frontier MO theory to arrive at a complete picture. The transition state models have several interesting properties: geometry, energy, electron distribution (in the form of potential maps and computed NAO charges). The models also allow several interesting comparisons: between regioisomeric transition states (same reactions), between favored transition states (different reactions), and between disfavored transition states (different reactions).

I would like your analysis to stand as your second “project” for this course, so please do a careful job, type your analysis, and don’t hesitate to ask for extra time if you need it. Do not do any additional calculations, however. You have the models you need.