Comparison of Theoretical and Experimental Studies of the Claisen Rearrangement

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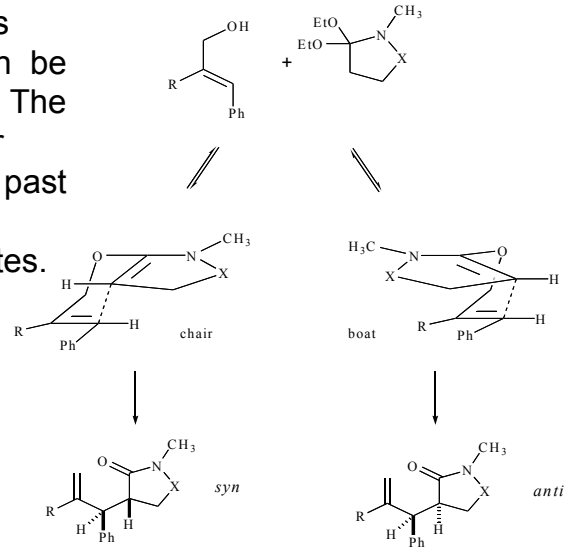
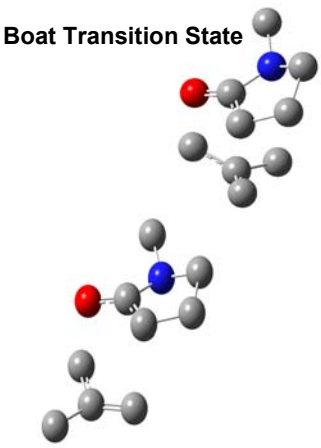
Objective: The Claisen Rearrangement is can proceed through either a chair or a boat transition state. The transition state determines the stereochemistry of the product, and can be modeled using density functional theory. The difference in the free energy between the chair and the boat can be compared to those of past experimental data. We hope to show that DFT can be used to accurately model transition states.

Method: The transition states are modeled with increasing complexity in Gaussian '03 and are optimized using a variety of functionals and basis sets. The Δ(G‡)'s of corresponding transition states were compared within each.

The Claisen Rearrangement





Results: The free energy of the transition states closest to those in the experimental data were compared. The experimental ΔG's were calculated using the Transition State Theory on previous product ratios. The most accurate functional seems to be the B3LYP in the 6-311G(d,p) basis set. Since all results were within 3 kcal/mol of the experimental quantities, we conclude that DFT is reasonably accurate at modeling transition states.

Comparison of Theoretical and Experimental Results for the Transition States shown.

Functional	Basis	Δ(G‡) (kcal/mol)
B3LYP	6-31G(d)	2.99
B3LYP	6-311G(d,p)	2.77
B3LYP	6-311+G(d,p)	2.87
MPW1PW91	6-31G(d)	4.25
MPW1K	6-31+G(d,p)	4.78
Experimental		1.82

Future Work: Our modeled transition states do not have the phenyl group that the experi-mental one's did, making their comparison no more than an estimate. If we are able to model the exact transition state from the experimental data, will the results be more accurate? What other functionals or basis sets may further increase our accuracy?

Funding: The Camille and Henry Dreyfus Foundation, Inc.