ISOTOPE EFFECTS, DYNAMIC EFFECTS AND MECHANISMS OF [2+2] CYCLOADDITIONS

A Dissertation

by

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Submitted to the Office of Graduate and Professional Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

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December 2013

Major Subject: Chemistry

ABSTRACT

In this dissertation, experimental probes and theoretical calculations have been applied to delineate mechanisms of various [2+2] cycloadditions. Besides common experimental observations and transition state theories, this dissertation focuses on the application of kinetic isotope effects (KIEs) and dynamic effects for a better understanding of the mechanisms.

The studies of dimerization of allene and [2+2] cycloaddition between 1,1-dimethyl allene and dimethyl maleate showed significant intramolecular KIEs and important reaction intermediates. These experimental observations strongly support a stepwise mechanism via a diradical intermediate. Based on this proposal, theoretical calculations gave excellent predictions of experimental observations. The controversy from previous literatures was well resolved by carefully analyzing the experimental observations.

Research on Lewis acid catalyzed [2+2] cycloaddition between allene and alkenes were conducted via a combination of product studies, experimental kinetic isotope effects, common theoretical calculations and quasiclassical trajectory simulations. The results identified two important dynamic effects in these reactions, the bifurcating energy surface and the non-statistical recrossing. These dynamic effects explained the inverse KIEs in the reaction between allene and tetramethylethylene and the regioselectivity in the reaction between allene and isopropylidenecyclohexane.

In stabilized Wittig olefination, the betaine was proposed to be an intermediate in the formation of the oxaphophetane as opposed to modern undertandings of a concerted mechanism. Experimental KIEs were consisted with a two-step mechanism and theoretical calculations located an intermediate along the reaction pathway. Trajectory simulations also showed significant amount of recrossing at the transition state and a possible hidden entropic intermediate in the reaction. These results provided a unique angle to understand the mechanism and the selectivity in the stabilized Wittig olefinations.

Dynamic effects not only play important roles in common organic reactions, but also in complicated enzynamic reactions, such as the transannular Diels-Alder reaction catalyzed by the corresponding “Diels-Alderase” SpnF. This reaction includes the role of a [6+4] cycloaddition, a bispericyclic transition state, a bifurcating energy surface, a dynamically stepwise cycloaddition, an entropically-delineated intermediate, and transition state recrossing in the mechanism. The reaction is not its caricature from classical mechanistic analysis and it is not well described by either concerted or stepwise labels. Instead, the mechanism is richer and can only be understood by consideration of dynamics.

DEDICATION

This dissertation is dedicated to my six years of persistence in Ph. D. studies, to my ten years of love in chemistry, to my everlasting curiosity to the scientific unknowns.

ACKNOWLEDGEMENTS

I would like to thank my committee chair, Dr. Singleton, and my committee members, Dr. Gladysz, Dr. Bergbreiter, and Dr. Cheng for their guidance and support throughout the course of my Ph.D. studies.

I also thank my friends and colleagues and the department faculty and staff for making my time at Texas A&M University a great experience. I also want to extend my gratitude to my lab mates for their supportive discussions and thoughtful suggestions.

Finally, thanks to my parents for their encouragement, patience and love.

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INTRODUCTION

Physical organic chemistry has advanced both experimentally and computationally in the past 50 years to unravel the mechanisms of various organic reactions. Early studies mainly utilized meticulous experimental designs, such as crossover experiments,[1-5] isotopic labeling[6-10] and trapping agents[11-15] to probe reaction mechanisms. These experimental studies have successfully set foundations for many organic reaction mechanisms and allowed chemists to improve and manipulate organic reactions to a great extent. As science and technologies had advanced along the course, instrumental analysis, such as NMRs, started to play important roles in mechanistic studies. However, experimental studies often require cautious designs and simplified systems to work with, which are often proven to be difficult or impractical, so they don't work well with complex systems and only provide qualitative ideas of a reaction mechanism. With the development of quantum chemistry and computational technology, chemists were able to use transition state theory (TST) and its close derivatives (e.g. variational TST) to model chemical reactions.[16-23] This allows us to quickly and quantitatively understand and predict reactivities and selectivities of chemical reactions. However, pure theoretical models based on hypothesis have to be verified experimentally otherwise they could be misleading in the real chemistry world. Fortunately physical organic chemists are able to employ both experimental and computational methods to understand reaction mechanisms and optimize reactions accordingly to develop reactions which are more synthetically useful.

Kinetic Isotope Effects

Kinetic isotope effects (KIEs) is one of the most useful experimental observations that reflect reaction mechanisms.[24-30] It shows that the substitution of an isotope in a molecule generally leads to rate changes in a chemical reaction. If the substituted atom is directly involved in the rate limiting bond changing process, it will result in a big change in the reaction rate, being referred as a primary isotope effect.[31-33] If the substituted atom is close to the atoms that are involved in a rate limiting bond changing process, it will result in a small change in the reaction rate, being referred as a secondary isotope effect.[34-36] Since these isotope effects are significant and closely associated with the bond changing process in organic reactions, they can be used as excellent probes to study reaction mechanisms. Substitution far away from the reacting center has a negligible influence on reaction rate and thus can be used as a standard when comparing the rate changes in isotopomeric reactions. Besides isotopic substitutions in reacting molecules, isotopic substitution in reaction media, i.e., solvents, can also lead to rate changes in a reaction. Solvent KIEs is also widely applied in studying reaction mechanisms in the corresponding media.[37-40]

The KIEs in a chemical reaction arises from many factors and thus is very complicated for a thorough understanding. Considering some basic assumptions, a qualitative explanation is given here. Suppose the isotopic substitution in molecules does not affect the potential energy surface or the electronic energies of the system, the KIEs are originated from the difference of the frequencies of the vibrational modes in different isotopomers, most importantly, the modes associated with a rate limiting bond changing process. In a given vibrational mode, heavier isotope will possess lower zero-point energy (ZPE) than the lighter isotope (Figure 1.1). The ZPE difference between the two isotopomeric vibrational modes depends on the shapes of their potential energy well: in a tight potential energy well, which is often representative for a reactant or intermediate's potential energy, the ZPE difference between two isotopomers is bigger than those in a loose potential energy well, which is often representative for a transition structure. Qualitatively, the ZPE difference between reactants and transition state is larger for heavier isotopomers (**ΔZPE (^{H}X)**), resulting in a slower reaction comparing with the lighter isotopomers (**ΔZPE (^{L}X)**).

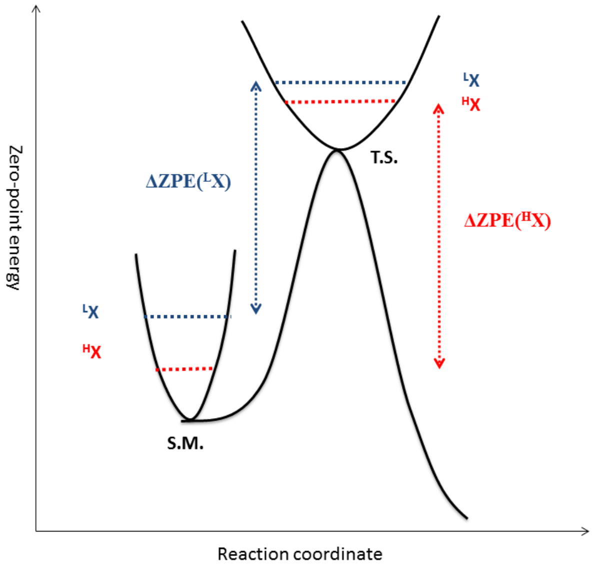


Figure 1.1. Zero-point energy of isotopomeric vibrational modes.

The most useful KIEs to study organic reactions are ^{2}H KIEs and ^{13}C KIEs. The rate change in a reaction from these isotopomers can be observed by various methods. Singleton has developed a general methodology for the simultaneous determination of

KIEs at multiple (possibly all) position in a molecule at natural abundance by NMR spectroscopy.[41] This method is applied in the measurements of intermolecular starting material KIEs, intermolecular product KIEs and intramolecular KIEs.

To measure intermolecular starting material KIEs, a reaction is taken to high conversion (ca. >80%), and the unreacted starting material is recovered from the reaction. Since heavier isotopomers reacts slower in a reaction, the recovered starting material will be enriched with heavier isotopes (^{2}H and ^{13}C). The abundance of these isotopes is measured by their corresponding NMR via a standard procedure.[41] A parallel NMR analysis of the original starting material (not subjected to reaction conditions) is also carried out as a standard. The relative isotopic composition (***R/R₀***) at each position in the molecule is determined by integrations for the peak of interest in the recovered material versus the standard. The KIE can then be calculated from ***R/R₀*** and the conversion (***F***) using the following equation.

$$KIE_{\mathrm{S}\_EXP} = \frac{\log(1-F)}{\log[(1-F)\times \mathrm{R/R_0}]}$$

Sometimes it is very difficult to recover the starting material from a reaction due to decomposition or instability of the starting material. In these cases, we can measure intermolecular product KIEs. In principle the KIEs in the reaction could be obtained from either analysis of recovered starting materials or analysis of the product. This method is subject to error because small departures from a true 100% conversion lead to relatively large errors in the KIEs, and 100% conversion of both reactants is difficult to achieve in a bimolecular stoichiometric reaction. To avoid this problem, the experimental design requires two reactions for each substance in a typical bimolecular reaction: one reaction taking starting material **A** to low conversion (***F***, *c.a.* ~20%) and the other starting material **B** to 100% conversion, the other one is vice versa. The low-conversion reaction for **A** serves as the 100%-conversion reaction standard for **B** and vice versa. The relative isotopic composition ***R/R₀*** is measured in a similar way to the intermolecular starting material KIEs case. The KIE is again determined by ***R/R₀*** and ***F*** using the following equation.

$$KIE_{P\_EXP} = \frac{\log(1-F)}{\log(1-F \times \mathrm{R/R_0})}$$

Intramolecular KIEs is a measurement of the relative reaction rate on equivalent positions in the starting material. Since the two positions are equivalent in the starting material but different in the product, the intramolecular KIEs reflect the product determining process. This has an advantage over intermolecular KIEs as it only requires products for the measurement. As a result it has minimal requirement of reaction yields as long as the product is stable and does not perform further transformations. The intramolecular KIEs is calculated based on the ratio of integrations for the peak of interests in the product, as shown in the following equation.

$$KIE_{INTRA} = \frac{R}{R_0}$$

A quantitative description of KIEs was proposed by Bigeleisen and Mayer in 1947, as shown in the following equations.[42]

$$KIE_{TST} = \frac{\nu_1^{\ddagger}}{\nu_2^{\ddagger}} \frac{(s_2/s_1)f_{GS}}{(s_2/s_1)f_{TS}}$$

$$(s_2/s_1)f_{GS} = \prod_i^{3N-6} \frac{\nu_{2i}}{\nu_{1i}} \frac{1-e^{-u_{1i}}}{1-e^{-u_{2i}}} \frac{e^{u_{1i}/2}}{e^{u_{2i}/2}}$$

$$u_i = h\nu_i / kT$$

$$(s_2/s_1)f_{TS} = \prod_i^{3N-7} \frac{\nu_{2i}}{\nu_{1i}} \frac{1-e^{-u_{1i}}}{1-e^{-u_{2i}}} \frac{e^{u_{1i}/2}}{e^{u_{2i}/2}}$$

The equation takes three factors into consideration, the temperature (**T**), the reduced isotopic partition function or the fractionation factor (**s2/s1**), and the frequency of the vibrational modes (**$\nu^{\neq}$**). This equation generally gives good predictions on experiments without significant tunneling.

Tunneling is the quantum mechanical process by which barriers can be traversed without sufficient activation energy. A full allowance for tunneling in all vibrational modes is too complicated so that only the modes associated with the reaction are considered. The barrier is treated as an infinite parabola with the curvature of the parabola defined by theoretical frequency calculations. The resulting one-dimensional tunneling correction is defined and applied to give a modified KIE.

$$KIE_{1D-tunneling-IP} = \frac{u_1^{\ddagger}/2\sin\left(u_1^{\ddagger}/2\right)}{u_2^{\ddagger}/2\sin\left(u_2^{\ddagger}/2\right)}$$

$$KIE_{calc} = KIE_{TST} \times KIE_{1D-tunneling-IP}$$

The full statistical mechanical treatment allows a quantitative calculation of the isotope effects. Such predictions have proven to be highly accurate in reactions not involving hydrogen transfer. In this way, the isotope effects may be used to compare with experimental results and examines the validity of proposed reaction mechanism.

Transition State Theory

Transition state theory is arguably the most useful theory to quantitatively understand the rate of a chemical reaction. In transition state theory, a reaction diagram is consisted of reactants, products and a dividing surface between the two, being referred as transition state. The transition state is not directly observable under experimental conditions but can be located computationally by searching for the first-order saddle point along the minimum energy pathway (MEP) between the reactant and the product on the potential energy surface of the reaction. Such saddle point is a minimum along all the other dimensions but a maximum along the reaction coordinate. The rate of a reaction at given temperature is determined by the free energy difference between the transition state and the reactants (Figure 1.2).

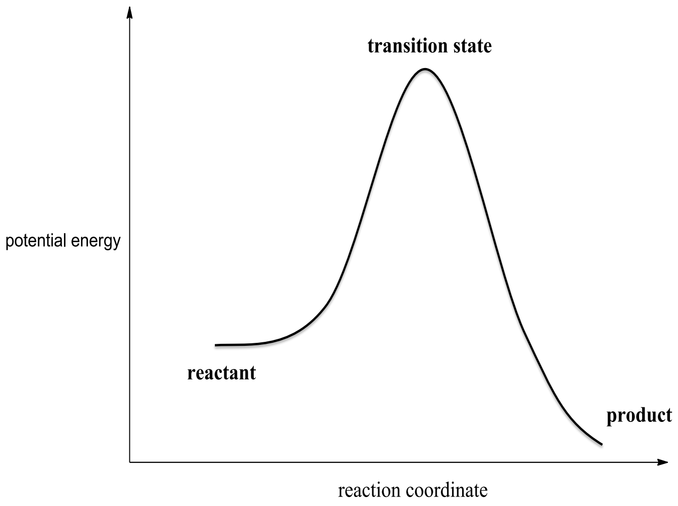


Figure 1.2. 1D representation of transition state theory.

Due to its simplicity and versatility, transition state theory has been widely applied to understand the kinetics in organic and enzymatic reactions, such as the KIEs. However, conventional transition state theory often falls short in predicting the absolute rate constant of chemical reactions, presumably due to two of its pre-assumptions. The first assumption is that the reaction follows classical mechanics instead of quantum mechanics-this ignores tunneling in reactions and thus often underestimates the rate of a reaction. The second assumption is that the trajectories starting from the reactants will pass through the transition state only once to form the products and never recross, which often overestimates the rate of reaction.

In a lot of cases, these two effects are minor and cancel out with each other so the prediction from conventional transition state theory still works. But in many other cases where one effect is more dominant, conventional transition state theory fails miserably to predict the observed rates of a reaction. Tunneling correction has been widely applied to provide better predictions in reactions that involve significant tunneling effect, i.e. proton transfer reactions that involves substantial hydrogen motion at the transition state, as we already discussed above. On the other hand, variational transition state theory[43] was developed to understand the reactions that have a lot of recrossing at the transition state.

In variational transition state theory, the transition state is placed along the minimum energy pathway (MEP) so that it minimizes the rate of the reaction. This suggests that the transition state is at the free energy maximum instead of potential energy maximum along the MEP. In a bonding process, entropy decreases as the bond forms and reaches its minimum after the bond completely formed. The corresponding free energy thus will increase as the bond forms and reaches its maximum after the potential energy maximum. Under the paradigm of conventional transition state theory, this can be recognized as that it requires not only two molecules colliding with enough momentum (potential energy), but also with proper orientation and conformation (entropy) for a reaction to happen. Two molecules colliding with adequate energy but improper orientations will fall apart, or recross. The entropy effect serves as a dynamic bottleneck after the transition state to control the rate of the reaction. Under the paradigm of variational transition state theory, this can be recognized as that the free energy maximum is often (not always) later than the potential energy maximum. After passing the variational transition state, trajectories will not go back to the reactants. The rate of the reaction then can be determined by the free energy differences between the variational transition state and the reactants (Figure 1.3).

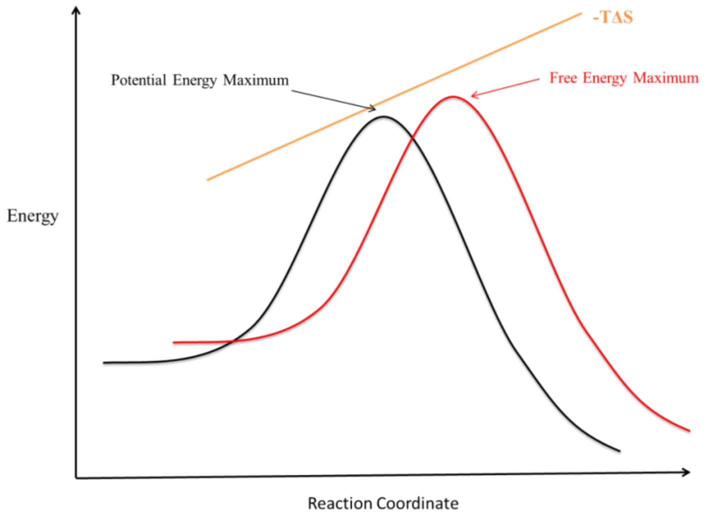


Figure 1.3. 1D representation of variational transition state theory.

Dynamic Effects

Transition state theories (TST) has been greatly applied and improved to understand the kinetics and thermodynamics in organic reactions. TST only considers the energies of specific points (i.e. starting materials, transition states and intermediates) along a reaction pathway to calculate the rate. The absolute rate of a reaction is determined based on the energy difference between the transition state and the starting material and the selectivity is determined based on the energy difference between the competing transition states. However, without explicit considerations of the shapes of energy surfaces and the motion and momenta of molecules passing through the transition state, it often fails in explaining and predicting experimental observations. In order to better understand the reaction mechanism, we have to take these factors into consideration, being referred as "Dynamic Effects".[44-49]

Bifurcating energy surface[50-52] is a special type of reaction energy surface, on which a single transition state connects one set of reactants with two or more sets of products. In these cases, instead of undergoing competing transition states and reaction pathways for different products, the reactants passes through one transition state and then follows separated paths afterwards to afford multiple products, that is the reaction pathway bifurcates after the initial transition state[53]. Such reactions are described as a two-step, no intermediate reaction, and exhibit unique dynamic effects. Selectivities of these reactions are governed by the shape of the energy surface rather than the transition state energetics.

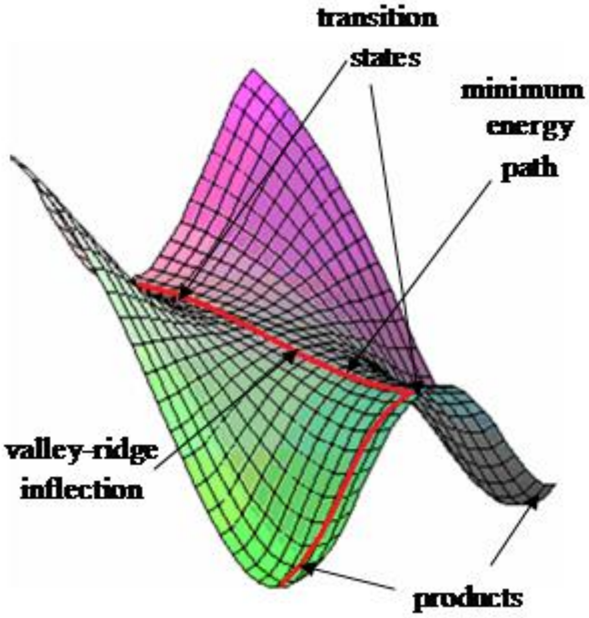
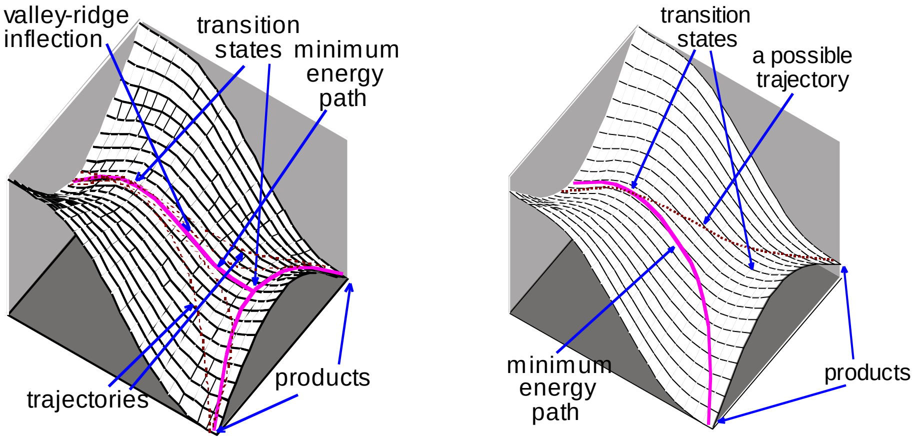


Figure 1.4. A qualitative depiction of a bifurcating energy surface.

The shape of the energy surface has an effect on the path taken by the starting materials. This is evident when one considers the intrinsic shape of a potential energy surface with two transition states connected by a minimum energy path. The initial rate-limiting transition state is in a valley which descends onto a ridge as it approaches the second transition state. This point is nominally the valley-ridge inflection (VRI) and is defined by the point on the minimum-energy path when curvature of a transverse mode passes from positive to zero on its way to negative. Past the valley-ridge inflection, the reaction path will bifurcate to different products (Figure 1.4).

The nature of a bifurcating potential energy surface can be of two types. The first of these is a symmetrical bifurcation in which both exit channels result in identical products (equal in energetics). The second type of potential energy surface is an unsymmetrical bifurcation which may lead to two different products with very different energies. Reactions involving an unsymmetrical bifurcating surface are a much more complicated case as it is very difficult to predict the product ratio and realize that the second possible product can be formed from the initial transition state (Figure 1.5).



(a)

(b)

Figure 1.5. Two different types of bifurcating energy surface.

Non-statistical recrossing[47, 49, 55, 56] is another type of dynamic effects. Although many transition state theory models have statistically predicted recrossing at reaction barriers, the effect of non-statistical recrossing is still under recognized. Molecules passing through a low potential energy barrier often encounters an entropic barrier shortly afterwards, as addressed in VTST, so sometimes instead of proceeding to form the products, molecules do reverse and return to the reactant side of the surface. The amount of recrossing depends on the shape of the energy surface, the position of the variational transition state and many other factors. VTST can only predict the recrossing effect statistically, without taking the detailed motion of molecules at the transition state into consideration. The non-statistical recrossing affects the rates and selectivities in many ordinary organic reactions and complicated enzymatic reactions. We have to consider the detailed motion and momenta of molecules passing through the reaction barrier and use trajectory simulations to provide in depth explanations and predictions for such dynamics effects (Figure 1.6).

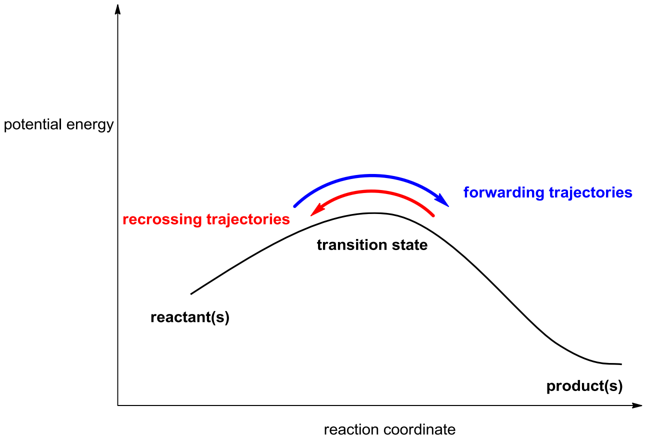


Figure 1.6. A qualitative depiction of transition state recrossing.

Non-statistical recrossing is essential to understand the reactivity of molecules at the transition state. Since currently there is no theory to completely predict and explain the non-statistical recrossing, experimental observations, such as KIEs, become very important to probe the recrossing and very valuable in identifying and understanding this dynamic effect. In a reaction involving significant amount of recrossing at the transition state, much smaller or even inverse KIEs were observed, in contrast to conventional transition state predictions.

Many other kinds of dynamic effects, such as incomplete vibrational energy redistribution (IVR) and Newtonian isotope effects have also played important roles in ordinary organic reactions.[47, 56] Possibly many more kinds of dynamic effects have not been revealed yet. The reactivity and selectivity of a reaction is not only governed by transition state theories but also affected by these complicated dynamics effects.

[2+2] Cycloaddition

The [2+2] cycloaddition is one of the principle strategies to synthesize cyclobutane and its derivatives.[57-61] It not only provides useful building blocks for complicated natural products, but also bears intrinsic mechanistic interests.[62-66] Photon-induced [2+2] cycloadditions have been well studied and applied as a powerful tool to synthesize cyclobutane rings effectively and selectively, even though that there are still some unrevealed details in the mechanisms. Thermal [2+2] cycloadditions, on the other hand, often requires harsh reaction conditions and suffers from low yields and selectivities due to its orbital symmetry restrictions and steric congestions. However, this reaction can happen stepwisely via either diradical or zwitterionic intermediates. More recently, transition-metal complexes have been playing a crucial rule in catalyzing [2+2] cycloadditions and thus promoted a lot of studies in these reactions. In the light of numerous precedencies, this dissertation will focus on a thorough understanding of various [2+2] cycloadditions.

There have been debates over the mechanism of thermal [2+2] cycloaddition involving allenic compounds-does this reaction happen asynchronously in a concerted antifacial fashion or stepwise involving a diradical intermediate? Early studies showed various experimental results supporting both sides. In 1970s, Dolbier and co-workers conducted a series of deuterium isotope studies on this reaction and concluded that the observed secondary deuterium isotope effect indicates this reaction proceeds stepwise via a bis-allyl radical intermediate.[67] Although Dolbier's work remarkably shed light on the mechanism of allene dimerization, it still failed to account for the high stereo specificity of 1,1-dichloroallene, as well as in many other cases.[68-69] As we have learned from previous studies, there might be a third possibility, which we described as an asynchronous process. The observed secondary deuterium isotope effect does not rule out this possibility, nor does other experimental observations. Another issue that Dolbier did not address on is that there are no direct experimental evidences of the diradical intermediate. Moreover, details about the geometry of transition states, intermediates and energy surface are not well defined. We hereby propose to use intramolecular primary ^{13}C isotope effects to probe the product determining step in this reaction, with the aid of high-level theoretical calculations. The intramolecular ^{13}C KIE arises from the first irreversible desymmetrizing step along the reaction coordinates, and reflects the "choice" that the intermediate makes to afford the final product. We are expecting a greater intramolecular KIEs if this reaction proceeds via a diradical intermediate compare to a concerted mechanism. We will also revisit the thermal [2+2] cycloaddition between 1,1-dimethyl allene and dimethyl maleate to understand the high stereospecificity in these reactions.

Thermal [2+2] cycloadditions can also proceed via a zwitterionic intermediate under mild conditions when electron rich alkenes react with electron poor alkenes, for example the cycloaddition between tetramethoxylethylene and tetracyanoethylene.[62] Lewis acids can catalyze these reactions by polarizing electron-poor alkenes, which makes it more prone to nucleophillic attack from electron-rich alkenes.[66] These reactions often afford regio and stereo isomers, and can become regio and stereoselective if chiral catalysts are present. While studies have been dedicated to design various catalysts to enhance the selectivity of these reactions, we are more interested in the origin of the regioselectivity of the reaction. We choose to study the cycloaddition between allene and electron-rich alkenes gain a better understanding of the mechanism and regioselectivity of the reaction.

Besides reaction between C=C bonds, [2+2] cycloadditions can happen between hetero atoms double bonds, for example between C=P and C=O, which is also known as Wittig olefination[70]. Wittig olefination is very useful in stereospecifically introducing C=C double bonds. This transformation combines carbonyl compounds, usually aldehydes or ketones, with phosphoranes (phosphorous ylides) to afford the corresponding olefins. The stereoselectivity of the reaction is generally determined by the type of ylides. Stabilized ylides, which have strong electron withdrawing substituents, i.e. ester groups, on the carbon, gives high E selectivity. Non-stabilized ylides, which has electron donating substituents, i.e. alkyl groups, gives high Z selectivity. Semi-stabilized ylides, which has moderate electron withdrawing substituents, i.e. aryl groups, gives poor stereoselectivity. Despite some debates over the detailed specific reaction substrates or conditions, a commonly accepted reaction mechanism involves an initial C-C bond formation between the carbonyl carbon and the negative charged carbon in the phosphorous ylide, and a following oxaphosphetane intermediate that leads to the olefin product. Previous studies have shown that the stereoselectivity of the reaction is affected by many factors such as the type of ylides, the polarity of the solvents, and the ions in the solutions. But more importantly, the transition state geometry is believed to account for the stereo outcome of Wittig olefinations.

A recent discovery of a key transannular Diels-Alder reaction in the biosynthesis of spinosyn A has promoted extensive studies towards its mechanism[71]. The traditional definition of a Diels-Alder reaction does not take into account of a number of complications in the mechanism that have come into light in recent years, especially with respect to the dynamics effects on the rate and selectivity. We present here the importance of such complications in the transannular Diels-Alder reaction catalyzed by SpnF, including the role of a bispericyclic transition state, a bifurcating energy surface, a dynamically stepwise cycloaddition, an entropically-delineated intermediate, transition state recrossing and a competing [6+4] cycloaddition in the mechanism. This reaction is not its caricature from classical mechanistic analysis and it is not well described by either concerted or stepwise labels. Instead, the mechanism is richer and can only be understood with consideration of dynamics.

Overall, the control of rates and selectivity of reactions are better understood when considering dynamic effects. With the help of experimental KIEs and trajectory simulations, mechanisms of various [2+2] cycloadditions and biosynthesis of spinosyn A are studied and understood based on dynamic effects.

ISOTOPE EFFECTS AND THE MECHANISM OF THERMAL [2+2] CYCLOADDITIONS INVOLVING ALLENIC COMPOUNDS

Introduction

Many useful theories have been developed to help chemists understand the mechanisms of organic reactions. The Woodward-Hoffman Rule, in particular, is one of the most valuable theories to qualitatively predict the possibility of pericyclic reactions based on the conservation of orbital symmetry.[72-73] A symmetry-allowed process, for example, a Diels-Alder reaction, can happen thermally in a concerted fashion, while a symmetry-forbidden process, such as a [2+2] cycloaddition, can take place thermally via a stepwise pathway. However, the [2+2] cycloaddition involving allenic compounds seems to be much more complicated to understand. Allenic compounds possess unique cumulative double bonds and thus may behave differently from ordinary alkenes in thermal [2+2] cycloadditions. There is experimental evidence that suggests a concerted mechanism in thermal [2+2] cycloadditions involving allenic compounds,[74] while other experiments pointed towards a stepwise mechanism via a diradial intermediate.[75] The mechanistic complexity in these reactions have inspired extensive research and led to important discoveries in this area.

In 1969, Thomas L. Jacobs found that the dimerization of chloroallenes (**2.1a**) was highly stereospecific.[76] Similarly, Edgar F. Kiefer found the thermal [2+2] cycloaddition between dimethyl allene (**2.1b**) and dimethyl fumarate had high stereospecificity[77] (Figure 2.1).

The observed high stereospecificity suggested a concerted mechanism in these [2+2] cycloadditions. The reaction is postulated to undergo an asynchronous [(π2a + π2s)allene +(π2s) alkene] interaction, which is also found in [2+2] cycloadditions between ketenes and alkenes.[78]

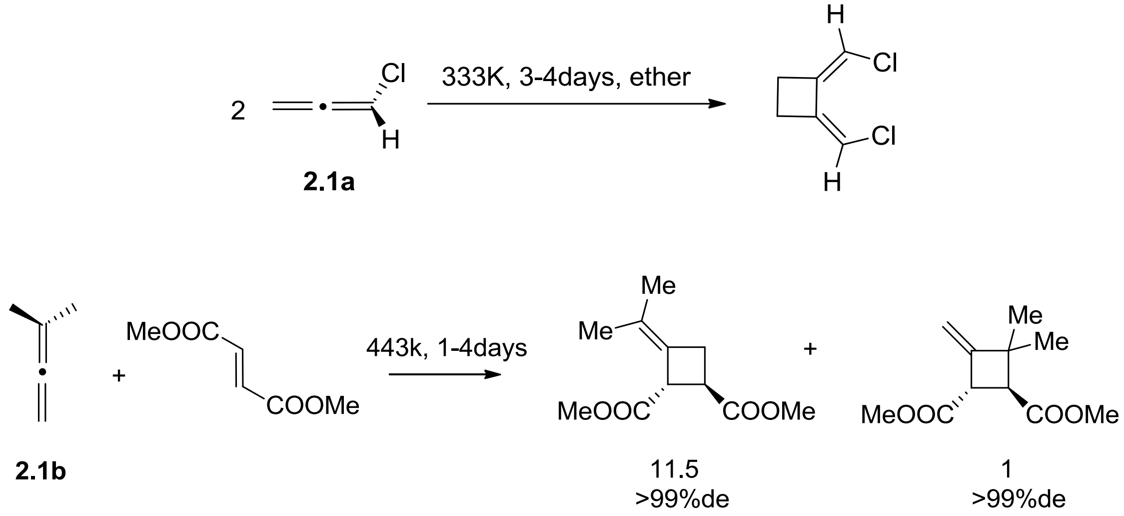
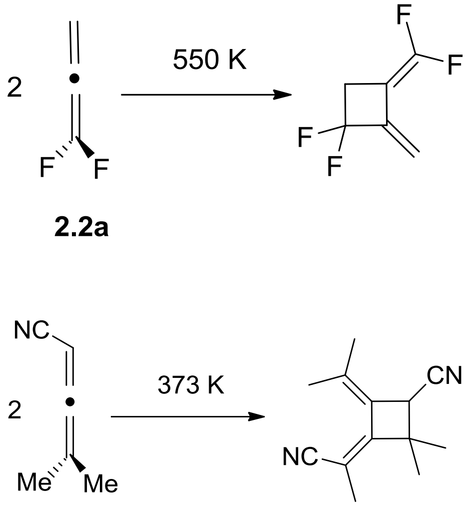


Figure 2.1. Experimental observations supporting a concerted [2+2] cycloaddition mechanism.

On the other hand, there are also experimental observations that argue against the concerted reaction pathway. For example, the 1,1-difluoroallene (**2.2a**) and 3,3-dimethyl-1-cyanoallene (**2.3a**) dimerize in a head-to-tail fashion.[79] These phenomena cannot be explained by a concerted process (Figure 2.2). Instead, the regioselectivity in these reactions are supportive of a stepwise process via a diradical intermediate.



2.2a

2.2b

Figure 2.2. Experimental observations for a stepwise [2+2] cycloaddition mechanism.

In 1970’s, Dolbier conducted a series of mechanistic studies in [2+2] cycloaddition involving allenes using experimental ^{2}H kinetic isotope effects.[80-82] Dolbier’s research showed that there is a preference of deuterium in the vinyl position over the allyl positions (allyl/vinyl=1.13 by ^{1}H NMR integration) in the product of allene dimerization (Figure 2.3).

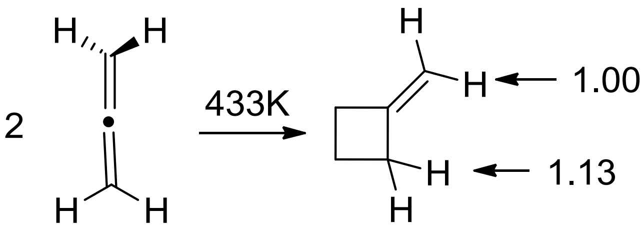


Figure 2.3. Dolbier’s Experimental Deuterium KIEs.

This experimental result also supports a stepwise mechanism involving a bis-allyl diradical intermediate. Although Dolbier's work has shed light on the mechanisms of allene dimerization, the deuterium KIEs did not match up with our intuitive predictions. The secondary deuterium isotope effect is usually interpreted based on the changes of out-of-plane C-H bending force constants, which is associated with the change of the hybridized state of the carbon. When a carbon changes from an sp^2 hybridized state to an sp^3 hybridized state, the secondary deuterium isotope effect tends to be inversed. But Dolbier's data showed normal secondary ^2H KIEs. Besides that, there is still no direct experimental evidence of a diradical intermediate in allenic [2+2] cycloadditions, and the origin of high stereospecificity in these reactions is not clear.

We hereby present a study of two [2+2] cycloadditions involving allenes to illustrate the mechanistic details using a combination of experimental ^{13}C KIEs and theoretical calculations. The results support the diradical stepwise reaction mechanism and provide a more careful interpretation of the high stereospecificity in thermal [2 + 2] cycloadditions involving allenic compounds.

Results

Isotope Effects of Allene Dimerization. Freshly prepared allene via dehalogenation of 2,3-dichloropropene was distilled and sealed into a thick wall glass tube as a benzene solution. Upon heating the solution at 140 °C for 14 hours, the reaction afforded approximately 5% of the desired product 1,2-dimethylene cyclobutane.

The ^{13}C KIEs for the dimerization of allene were determined by NMR methodology at natural abundance. The desired product was collected by fractional distillation of the combined crude product solution at 35 °C and analyzed by ^{13}C NMR. The relative isotopic compositions in the vinyl and allyl carbons were determined based on their ^{13}C signal integrations. The experimental results are summarized in Figure 2.4.

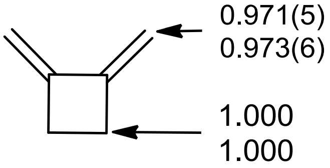


Figure 2.4. Relative ^{12}C ratios in two independent reactions of allene dimerization.

[2+2] Cycloaddition between 1,1-Dimethyl Allene and Dimethyl Maleate. 1,1-dimethyl allene and dimethyl maleate were dissolved in benzene and sealed in a thick wall glass tube. The reaction mixture was heated at 190 °C for 72 hours and afforded 8% desired product mixture of dimethyl 3-(propan-2-ylidene)cyclobutane-1,2-dicarboxylate (**2.5a**), dimethyl 3,3-dimethyl-4-methylenecyclobutane-1,2-dicarboxylate (**2.5b**) and 0.5% dimethyl 2-(3-methylbut-2-en-2-yl)maleate (**2.5c**). (Figure 2.5)

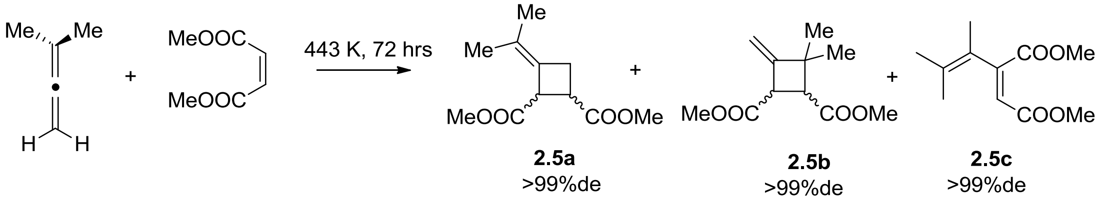


Figure 2.5. [2+2] cycloaddition between 1, 1-dimethyl allene and dimethyl maleate.

Theoretical Calculations. The mechanism of allene dimerization was studied in CASSCF calculations using 6-31G* and 6-31+G** basis sets with full geometry optimization in all cases. The involvement of diradical species limits the reliability of a computational mechanistic study of this reaction by itself, but consideration of the experimental isotope effects allows assessment of the theoretical predictions. In turn, the prediction of isotope effects from the theoretical models facilitates a detailed interpretation of the experimental isotope effects.

The ^{13}C and ^{2}H KIEs associated with the transition structures were predicted from the scaled theoretical vibrational frequencies using conventional transition state theory by the method developed by Bigeleisen and Mayer. Tunneling corrections were applied using the one-dimensional infinite parabolic barrier model. Such KIE predictions have proven to be highly accurate in reactions not involving hydrogen transfer.

The energy diagram of the reaction between 1,1-dimethyl allene and dimethyl maleate was computed with GAUSSIAN09. All structures were optimized and examined using standard frequency analysis at the level of (U)B3LYP/6-31G* theory. Theoretical calculations support a stepwise mechanism for this reaction.

Discussion

Due to the harsh reaction conditions in allene dimerization, it is difficult to directly monitor the intermediacy of the diradical species (if there is any). In order to distinguish a stepwise process from a concerted one, intramolecular ^{13}C KIEs were applied. In the allene dimerization process, if the reaction happens in a concerted fashion, the transition state for product formation is symmetrical with regards to the two terminal carbons in the allene, thus the relative ^{13}C composition on the allyl and the vinyl carbon in the product should be the same, which will give an intramolecular KIE of unity. On the other hand, if the reaction happens in two steps via a bis-allyl diradical intermediate, the two terminal carbons in the allene will no longer be equivalent at the transition state of second C-C bond formation. The second C-C bond formation would desymmetrize the system and lead to significant intramolecular KIEs between the allyl and vinyl carbon in the final product.

Experimentally we observed intramolecular KIEs of 1.030 in favor of the vinyl carbon over the allyl carbon in the final product. The KIEs showed that there is a preference of ^{12}C over ^{13}C in the second C-C bond formation, which is in agreement with a two-step mechanism (Figure 2.6). The first step is the C-C bond formation between two central carbons of the allene (**2.6a**), the resulting diradical intermediate (**2.6b**) then can rotate along the initially formed C-C bond to the appropriate conformation (**2.6c**) to form the second C-C bond between two terminal carbons of allene and afford the final product (**2.6d**). Along the reaction pathway, the two terminal carbons on one allene molecule are equivalent until the second C-C bond forms, where the intramolecular KIEs arise.

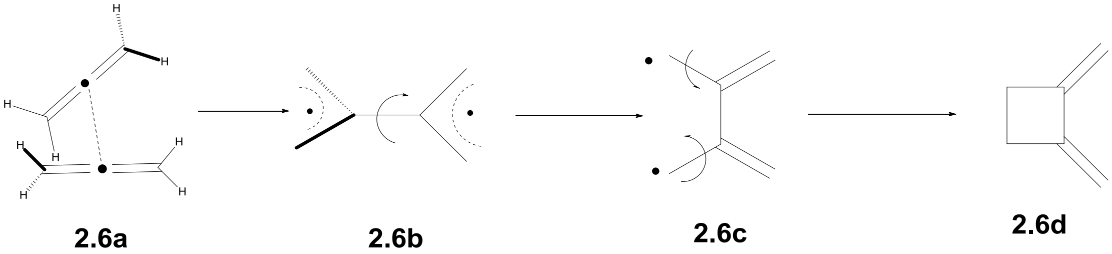


Figure 2.6. Allene dimerization via a bis-allyl radical intermediate pathway.

Theoretical calculations also suggest a stepwise mechanism in allene dimerization. All attempts to locate a concerted [2+2] transition state were not successful. Instead, two separated transition states were found with respect to the two C-C bond formations (Figure 2.7). The first C-C bond is formed between the two central carbons of allene when two allene molecules approach orthogonally to each other (**TS1**). The resulting intermediate (**INT1**) then rotates either conrotatorily or disrotatorily to adapt a proper conformation (**INT2**), which then undergoes the second C-C bond formation (**TS2**). There is also a small barrier (**TSr**) associated with the rotation process which connects two conformations of the diradical intermediate. The reality may be more complicated that this process, because there are many feasible conformation for the intermediate in this reaction. However, this model sufficiently depicts the two step process regardless of the conformational changes of the intermediate. This model is consistent with literature precedences as well as experimental results. The first C-C bond formation has a higher energy barrier and thus is the rate limiting step, while the second C-C bond formation desymmetrizes two terminal carbons in the allene and thus is the product determining step.

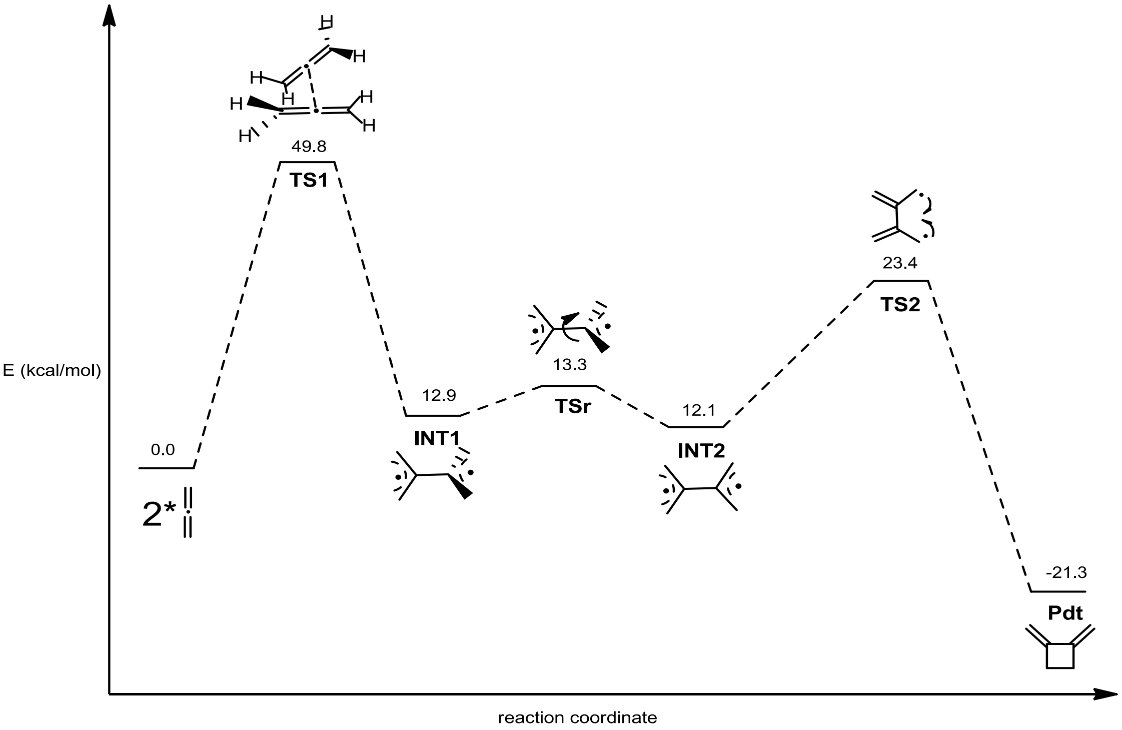


Figure 2.7. Calculated energy profile for allene dimerization using CASSCF (8, 8)/6-31+G**.

The predicated intramolecular KIEs based on the second transition state agree well with experimental data (Figure 2.8). The preference of ^{12}C over ^{13}C in the product determining step can be interpreted normally by the zero-point energy difference within the two isotopomeric vibrational modes at the transition states. The secondary ^{2}H KIEs, although against our initial expectations, turn out to be normal and consistent with Dobhier's experimental result. The diradical character of the transition states limits the accuracy of theoretical predictions, so the calculated KIEs were a little bit lower than the experimental numbers, but they both support the stepwise mechanism.

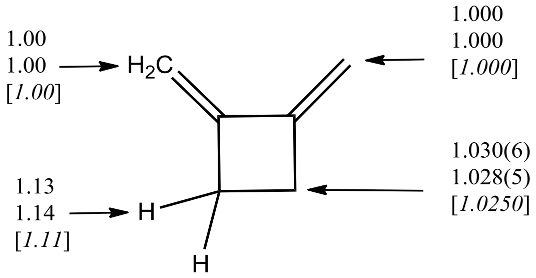


Figure 2.8. Experimental intramolecular ^{13}C and ^{2}H KIEs in 1, 2-dimethelenecyclobutane and theoretical predictions (in brackets and italicized) based on **TS2** using CASSCF (8, 8)/6-31+G**.

The cycloaddition between dimethyl allene and dimethyl maleate was previously reported by Edgar F. Kiefer in 1969. However when we revisited this reaction, we found out that the outcome of the reaction was much more complicated than what literature reported (Figure 2.9). The products were mainly consisted of the main stereospecific [2+2] cycloadducts (>95% in both **2.9p1** and **2.9p2**), some stereo scrambled cycloadducts (<5% in both **2.9p1** and **2.9p2**), and more interestingly, a very small amount of dimethyl 2-(3-methylbut-2-en-2-yl) maleate (**2.9bp**). This product was not recognized in previous studies yet provided very important details about the reaction mechanism. It is very difficult to explain the formation of this product based on a concerted mechanism of this reaction. Instead, a plausible explanation of the formation of this product involves a formation of the diradical intermediate (**2.9int**) and a [1, 3]-H shift (**TSh**). **2.9bp** served as an excellent evidence for the formation of the intermediate **2.9int**.

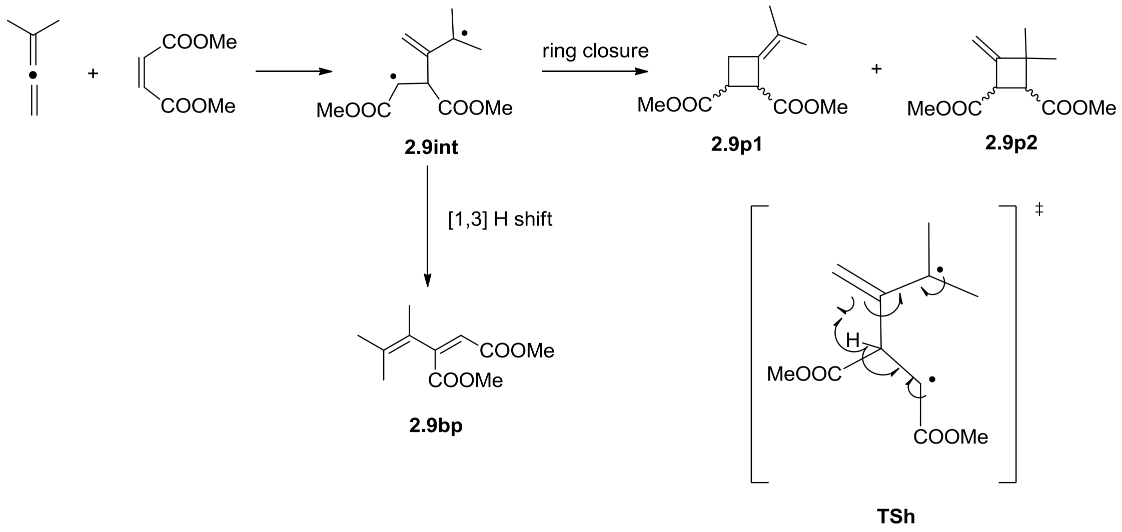


Figure 2.9. Mechanism of [2+2] cycloaddition between 1, 1-dimethyl allene and dimethyl maleate.

Theoretical modeling was performed to verify this mechanism (Figure 2.10). The calculated barrier for the second step of cycloaddition is higher than the first step, making it rate limiting. The **TSh** was found to be in comparable energy (slightly higher) with the ring closure step of the [2+2] cycloaddition. This supports that the [1,3]-H shift was a competing pathway from **2.9int**. Although being energetically disfavored, the **2.9bp** was still formed and observed under reaction conditions. It provided important evidence for the stepwise mechanism and the intermediacy of the diradical.

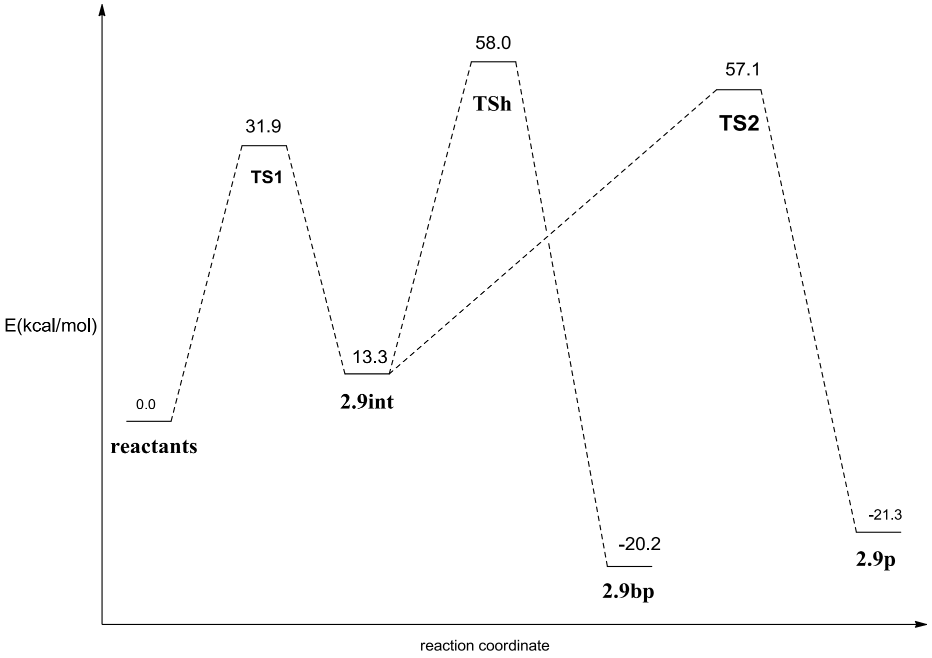


Figure 2.10. Calculated energy profile for of [2+2] cycloaddition between 1, 1-dimethyl allene and dimethyl maleate using UB3LYP/6-31G*.

As previously reported, the experimental outcome was indeed highly stereospecific, however the interpretation of this observation is not as straightforward as it seemed to be. This observation only suggests that there is no diradical intermediate on the time scale of a C-C bond rotation. In other words, if the intermediate is short-lived and reacts before a C-C rotates, the reaction could still be highly stereospecific. The average time for a C-C bond rotation is around 100 fs, but in this particular case, the average lifetime for the diradical intermediate is much shorter, only 53 fs based on trajectory simulations. This explains that although it goes through a diradical intermediate, the reaction could still be highly stereospecific.

Conclusion

Based on our studies on dimerization of allene and [2+2] cycloaddition between 1,1-dimethyl allene and dimethyl maleate, we are able to propose a stepwise mechanism for both reactions. Various experimental and theoretical evidences support the involvement of a diradical intermediate in these reactions. In the dimerization of allene, we observed an intramolecular ^{13}C KIE of 1.030 in favor of the vinyl carbon over the allyl carbon in the product. This observation supports the intermediacy of a bis-allyl diradical and can be understood based on a stepwise mechanism model. Theoretical modeling using CASSCF(8.8)/6-31+G** also supports this proposal and gave good KIE predictions based on the stepwise mechanism. The concerted [2+2] transition state was not located on the potential energy surface.

In the [2+2] cycloaddition between 1,1-dimethyl allene and dimethyl maleate, we observed and characterized an important byproduct from the reaction, which was presumably generated from the diradical intermediate. The high stereospecificity in this reaction should be interpreted more carefully. It only indicates that there is no intermediate within the resolution of C-C bond rotation time scale. In this particular case, the intermediate is short-lived and reacts before C-C bond rotates, so the reaction is still highly stereospecific with a diradical intermediate. Computed energy profile of this reaction is consistent with this mechanism and experimental observations.

In conclusion, the combination of experimental and theoretical studies supports a stepwise mechanism in thermal [2+2] cycloadditions involving allenic compounds. The postulated concerted process is not feasible due to its symmetry-forbidden nature and is not consistent with experimental observations.

Experimental Section

Allene Preparation. Adapting a literature procedure,[67] a three-necked round bottom flask was equipped with a magnetic stirrer, a 100 mL pressure-equalizing addition funnel and a coil condenser. The exit from the condenser was connected to an efficient trap of 100 mL capacity in a dry ice-acetone bath. A mixture of 95% ethanol: water (5:1 v/v) and 30 g (461.5 mmol) of zinc dust was added to the reaction flask. The addition funnel was filled with 25.5 mL (26 g, 236.2 mmol) of 2,3-dichloropropene. The mixture was stirred and heated to reflux, and then the 2,3-dichloropropene was added dropwise in 2-3 h at such a rate that reflux was maintained without external heating. After the addition was completed, heating was resumed for 1 h. The trap was then slowly warmed up to room temperature and the allene was purged with a very slow stream of nitrogen to a collecting thick-wall glass tube cooled by the dry ice-acetone bath.

Allene Dimerization. Adapting a literature procedure,[67] to a 100 mL thick wall glass tube were adding 5 mL of benzene and allene to its saturation via vacuum line. After deoxygenated and sealed in vacuum, the tube was wrapped with glass wool and heated at 140 °C for 14 h. The unreacted allene was then removed via vacuum line from -35 °C to 25 °C. The residue was collected and characterized by ^{1}H and ^{13}C NMR, 90% of which was found to be 1,2-dimethylenecyclobutane.

NMR Analysis of 1,2-Dimethylenecyclobutane. All NMR samples consisted of 200 mg of the substrate in 5 mm NMR tubes filled to a constant height of 5 cm with C_6D_6. The ^{13}C spectra were recorded at 125.81 MHz using inverse gated decoupling, 96 s delays between calibrated $\pi/2$ pulses, and a 7 s acquisition time. Integrations were numerically determined using a constant integration region for each peak. A zero-order baseline correction was generally applied, but to avoid any qualitative manipulation no first-order or higher-order baseline correction was ever applied. Twelve spectra were recorded for each sample. The integration value of each peak was determined by the average of all measurements. The uncertainty of the measurement was determined by considering a two-side 95% confidence interval in a T-distribution.

[2+2] Cycloaddition between 1,1-Dimethyl Allene and Dimethyl Maleate: Adapting a literature procedure,[77] to a 50 mL thick wall glass flask were added 1 g (1 equiv, 14.7 mmol) of 1,1-dimethyl allene and 2.2 g (1.2 equiv, 17.4 mmol) of dimethyl maleate, followed by 20 mL of benzene as solvent. The reaction mixture was stirred at 190 °C for

72 h in an oil bath. After reaction completed, the flask was cooled down to room temperature and the reaction mixture was then distilled at 100 °C under reduced pressure (30 mmHg) to remove most of the unreacted dimethyl maleate. The residue was then chromatographed on a 12"×36 mm silica gel column using using 15% ethyl acetate in hexanes as eluent to afford 0.02 g (0.6%) dimethyl 2-(3-methylbut-2-en-2-yl) maleate. NMR (δ (ppm), $CDCl_3$): ^{1}H (500 MHz): 6.62 (m, 1H), 3.85 (s, 3H), 3.76 (s, 3H), 2.12 (s, 3H), 2.07 (s, 3H), 1.62 (s, 3H). ^{13}C (125 MHz): 166.5, 147.6, 130.6, 129.7, 109.4, 55.0, 24.3, 15.8.

ISOTOPE EFFECTS, DYNAMICS AND MECHANISMS OF LEWIS ACID CATALYZED [2+2] CYCLOADDITION BETWEEN ALLENE AND ALKENES

Introduction

[2+2] cycloaddition is a straightforward and efficient method to build cyclobutane moieties in organic transformations.[83-86] However, its application in organic synthesis is limited due to orbital symmetry restrictions and steric congestions. The thermal concerted [2+2] cycloaddition is a symmetry-forbidden process and thus has very high reaction barrier, which eventually results in lower yield and selectivity.[87-90] The symmetry-allowed photo chemical [2+2] cycloaddition, on the other hand, is synthetically useful mostly in intramolecular reactions only and often requires special apparatus.[91-97] In order to fully utilize the efficiency and simplicity of [2+2] cycloadditions, chemists have tried various catalysts and substrates to facilitate the reaction. Lewis acid catalyzed [2+2] cycloadditions between allenes and alkenes, in particular, has been proved to be very successful in synthesizing methylene cyclobutane moieties.[98-105] While most attention has been drawn to develop catalysts for better regio and stereo selectivies in these reactions, the mechanism was not as well recognized. Despite some non-conclusive evidence for a concerted pathway in previous studies,[106] the mechanism is believed to be stepwise via a zwitterionic intermediate.[107-110] This proposed mechanism was widely accepted and studied to design effective lewis catalyst and to advance the stereoselective versions of the [2+2] cycloadditions (Figure 3.1).

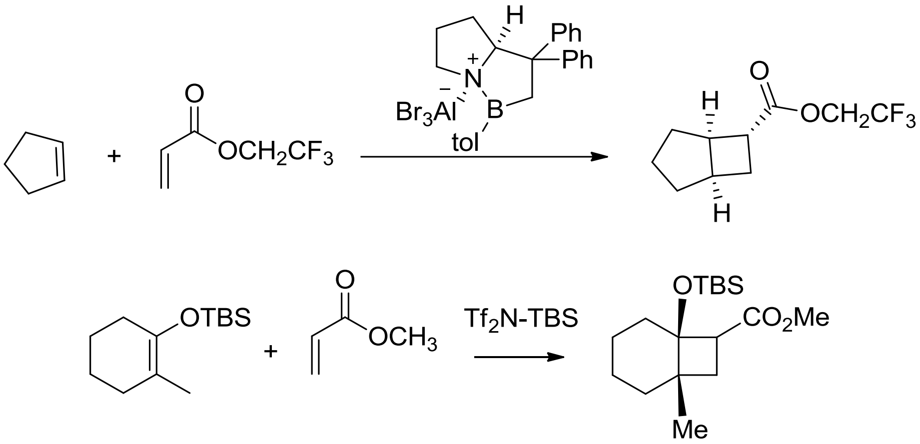


Figure 3.1. Examples for Lewis acid catalyzed stereo-selective [2+2] reactions.

From a mechanistic point of view, these reactions bear unique interests because it has exhibited several dynamic effects, such as bifurcating energy surface and non-statistical recrossing. Generally speaking, the effects influencing the selectivity between products may be artificially divided into different factors, for instance, the shape of the energy surface and the momenta of molecules passing through the transition structure (Figure 3.2). These factors are much less considered and understood in conventional transition state theory, but they can affect the reactivity and selectivity of the reaction. On a bifurcation energy surface, the selectivity is no longer governed by the energy difference between competing transition states. The momentum of molecules passing the transition state can affect the reaction rate because it can cause non-statistical recrossing. These dynamic effects need to be addressed and understood to gain better insights of the lewis acid catalyzed [2+2] cycloaddition.

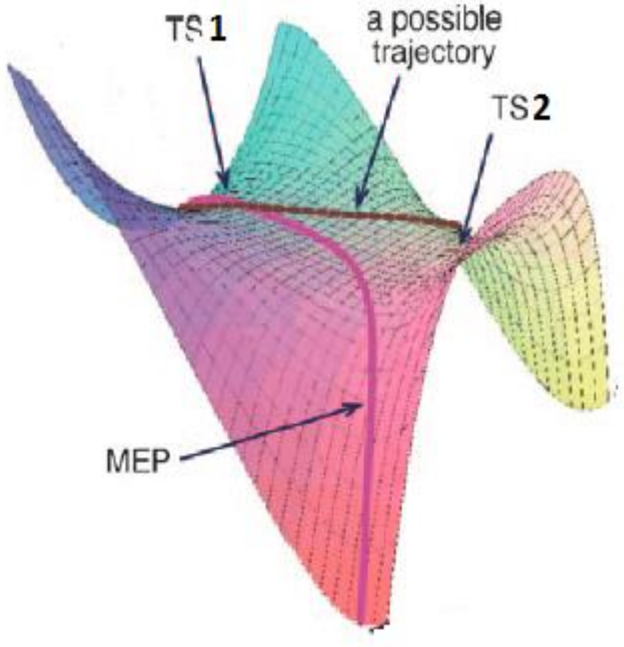


Figure 3.2. A qualitative description of bifurcating energy surface.

In 1975, Lucas and *et al* reported a [2+2] cycloaddition between allene and tetramethyl ethylene catalyzed by ethyl aluminum dichloride ($EtAlCl_2$, **3.3a**). [111] This reaction was proposed to undergo through a stepwise pathway via a zwitter ionic intermediate (**3.3b**). The catalyst coordinates to the double bond of allene, making it more electronically deficient and the central carbon prone to nucleophilic attack from the tetramethyl ethylene. The resulting intermediate (**3.3b**) can close the ring to afford the final product (**3.3c**). This reaction is simple and clean for us to use intramolecular kinetic isotope effects to study the mechanism. Furthermore, slightly unsymmetrical (pseudo-symmetrical) alkenes are used in this reaction to probe the regio-selectivity in this reaction (Figure 3.3).

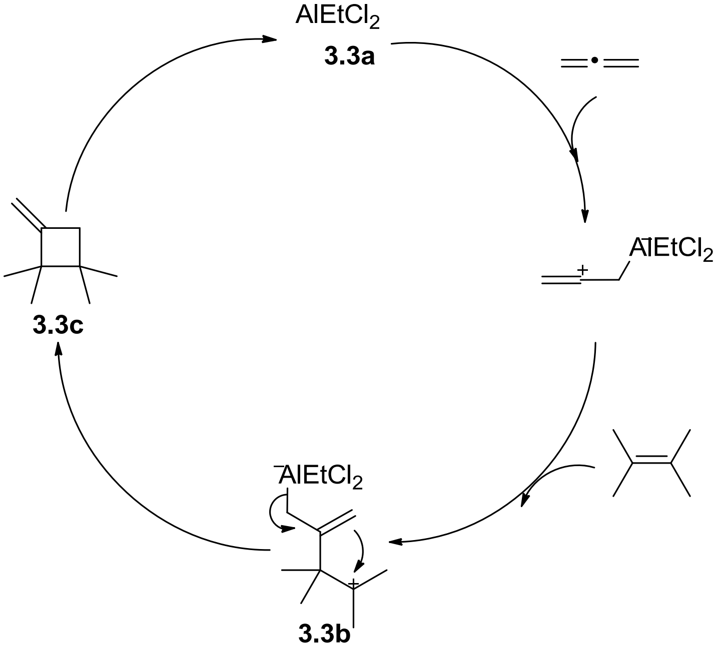


Figure 3.3. Proposed mechanism for [2+2] cycloaddition between allene and tetramethyl ethylene catalyzed by ethyl aluminum dichloride.

We hereby present a study of the mechanisms of [2+2] cycloadditions between allene and alkenes using a combination of product studies, experimental kinetic isotope effects, common theoretical calculations and quasiclassical trajectory studies. The results show that the cycloaddition between allene and alkenes catalyzed by lewis acid exhibits complex dynamic effects. This reaction has significant non-statistical recrossing at the initial transition state and a bifurcation energy surface after that. The stereoselectivity of the reaction is not determined by the transition state energetics; instead it is controlled by the detailed motion of molecules passing through the transition state and the shape of the potential energy surface.

Results

Cycloaddition between allene and tetramethylethylene. This reaction was catalyzed by 5% ethyl aluminum dichloride in dichlorobenzene proceeds smoothly to give nearly quantitative yield of the desired product, despite of some oligomer formation. This reaction was studied using intramolecular ^{13}C KIEs in the product. Two such KIEs may be observed depending on whether the ^{13}C was in the allylic (**C2**) or homo allylic carbons (**C3**) of the product. These KIEs were determined at natural abundance by NMR methodology. A total of 12 KIE measurements were made on samples of the product obtained from two independent reactions at 0 °C. The intramolecular KIE is 1.008 in favor of the homo allylic carbon (**C2**) in the product (Figure 3.4).

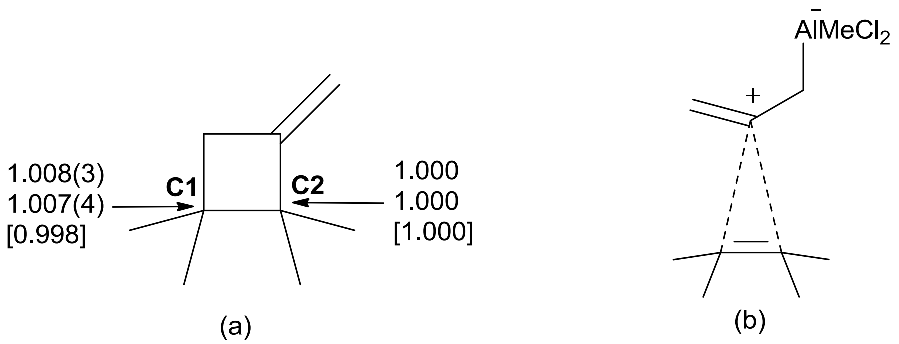
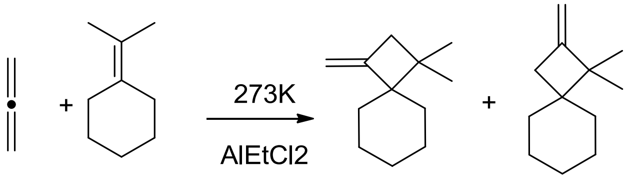


Figure 3.4. (a) Experimental intramolecular ^{13}C KIEs of 1,1,2,2-tetramethyl-3-methylenecyclobutane and theoretical intramolecular ^{13}C KIEs (in brackets and italicized) based on transition structure (b) using M06/6-31+G* PCM model (b) Transition structure of the first carbon-carbon bond formation.

Cycloaddition between allene and isopropylidenecyclohaxne. This reaction was catalyzed by 2-5% ethyl aluminum dichloride in difluorobenzene proceeds smoothly to give around 80% yield of the desired two regio-isomers: 1,1-dimethyl-3-

methylenespiro[3.5]nonane(**3.5p1**) and 1,1-dimethyl-2-methylenespiro[3.5]nonane (**3.5p2**). The two isomers are distilled and characterized by ^{1}H, and ^{13}C NMR and 2D NMRs to determine their relative ratios (Figure 3.5).



3.5p1:57% **3.5p2**: 43%

Figure 3.5. [2+2] cycloaddition between allene and propan-2-ylidenecyclohexane catalyzed by ethyl aluminum dichloride.

Calculations of structures, energies, and frequencies were performed by standard procedures in Gaussian09 (S1) unless otherwise noted. The mechanism of [2+2] cycloaddition was studied in B3LYP/M062X using 6-31G* and 6-31+G** basis sets with full geometry optimization both in gas phase and in a continuum solvent model.

Quassiclassical trajectories simulations were employed to model the dynamics in these reactions. The desired energy in each of the normal modes was mapped from a random number generator to a Boltzmann distribution. The phase of each of the normal modes was mapped from Gaussian distribution of random numbers. This distribution is not correct for a classical oscillator but would be approximately correct for a quantum oscillator in its ground state (only ignoring mode displacements outside of the classical limit), and has the advantage that a larger portion of the trajectories start with an energy approximating the initially desired energy. Because of the inharmonicity of the lowest-energy modes, the choice of a random phase for these modes led to a problem for the trajectories using the larger alkyl groups, as the energy of the starting point structure for trajectories would inevitably be far from its desired value. Gaussian09 was used to calculate the forces at each point in trajectories. The original version of this program was published in the appendix of this dissertation.

Discussion

The experimental KIE is quite astonishing to us as it showed an inverse primary ^{13}C isotope effect. Based on transition state theory, this experimental KIE showed that the initial carbon-carbon bond formation is less likely to be product determining because it would have shown a normal primary ^{13}C KIE. We propose here a C_2 symmetrical transition state (Figure 3.4 (b)) for the initial carbon-carbon bond formation. Since this transition state can lead two possible isomeric products, this reaction has a bifurcation energy surface.

A careful examination with the KIEs leads to another interesting question, why the KIEs are inverse? We have observed this interesting phenomenon in some ketene reactions, yet it is the first time we observe this in [2+2] additions between olefins. In order to fully understand this observation, we need to consider the dynamics effects in this reaction, particularly the non-statistical recrossing.

Normally we attribute the kinetic isotope effect to the zero-point energy difference of the vibrational modes in isotopomers, As heavier isotopomers react slower to afford the product, they recross slower back to starting material as well. If the reaction involves significant amount of recrossing at the transition state, light isotopomers (^{12}C) will reverse to starting materials quicker and to a greater extent, while heavier isotopomers (^{13}C) move slowly towards the product with less reversibility. As a result, the intramolecular KIEs in the final product are inverse.

To test this hypothesis, we did trajectory simulations this system, and the results are quite striking. This reaction has a very high (40%) recrossing possibility compared to normal organic reactions. When take a closer look at those trajectories that recrossed, we found out that recrossing happened more in heavier isotopomers than lighter isotopemers. If an in silico ^{140}C substitutes a carbon on the double bond of tetramethyl ethylene, 90% of the recrossing happened when the central carbon of allene is trying to form a bond with ^{12}C. This result is consistent with our hypothesis in non-statistical recrossing, that heavier isotope recrosses slower than lighter isotope. Quantitative predictions of the isotope effect can be made if we use adequate amount of trajectories and in silico heavy isotopic substitutions (Figure 3.6).

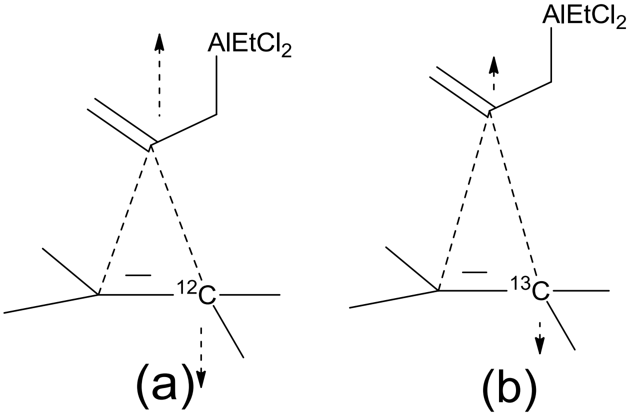
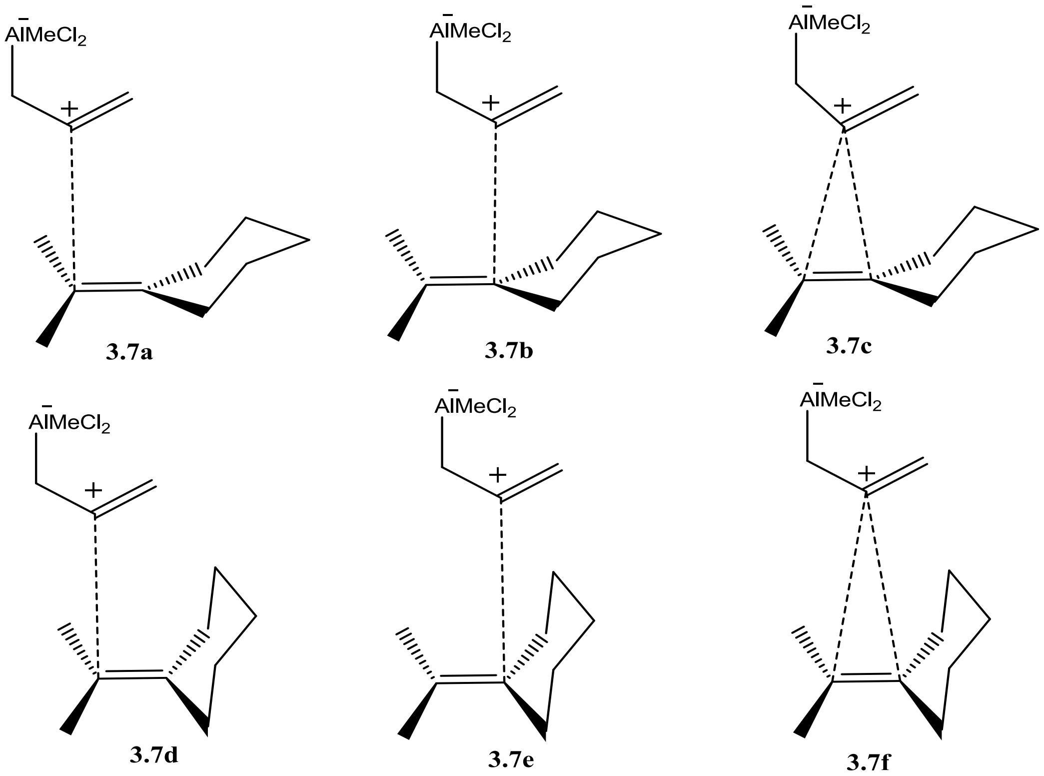


Figure 3.6. Qualitative depiction of recrossing at the first transition state (a) ^{12}C reacts and re-crosses faster (b) ^{13}C reacts and re-crosses slower.

Similarly, the [2+2] cycloaddition between allene and pseudo-symmetrical alkenes under this reaction condition should proceed via this mechanism. Again under these circumstances, transition state theory cannot predict the regioselectivity, because there are no competing transition states for different regio isomers. There is only one common transition state as the allene approaches the alkene in between the two carbons of the double bond (Figure 3.7).



3.7a **3.7b** **3.7c**

3.7d **3.7e** **3.7f**

Figure 3.7. Different Transition structures of the initial carbon-carbon bond formation between allene and isopropylidenecyclohexane. **3.7a-b**, **3.7d-e** are not found on the reaction pathway. Only **3.7c** and **3.7f** are located and they represent the axial attack and equatorial attack from the allene to the cyclohexane respectively.

The regio isomer came from the bifurcating pathways after the transition state. On the other hand, starting from the pseudo-symmetrical transition state, trajectory simulations successfully predict the product ratio to a good accurate extent. Experimentally observed products ratio was 57:43, and the trajectory simulations gave 186:135 (ca. 58:42). This result shows that our model of bifurcation energy surface describes well this [2+2] cycloaddition and can successfully predict the regioselectivity in this reaction.

Conclusion

Based on our studies of [2+2] cycloadditions between allene and alkenes catalyzed by lewis acid, transition state theory cannot account for the experimental KIEs and regioselectivities observed in these reactions. Instead, dynamic effects are more essential to understand the reaction mechanisms. Various experimental and theoretical evidences support the involvement of a bifurcation energy surface and non-statistical recrossing in these reactions. In [2+2] cycloaddition between allene and tetramethylethylene, an inverse ^{13}C is understood based on the hypothesis that heavy isotopes recross slower at the transition state, and this hypothesis is verified by our quasi-classical trajectory simulations. In [2+2] cycloaddition between allene and isopropylidenecyclohexane, the regioselectivity is understood based on the shape of a bifurcation energy surface and the motion and momenta of molecules passing through the transition state. This proposal was supported by trajectory studies and experimental observations.

In conclusion, conventional transition state theory is not capable of explaining the isotope effects and regioselectivity in Lewis acid catalyzed [2+2] cycloadditions. The consideration of dynamic effects, on the other hand, successfully predicts the experimental observations and provides detailed understanding of the regioselectivity in these reactions.

Experimental Section

Cycloaddition between Allene and Tetramethylethylene. The following compounds were consecutively dissolved in 20 mL of 1,2-dichlorobenzene under nitrogen gas at 25 °C: 1. Allene to its saturation *(ca.* 1 g, 25 mmol per 20 mL 1,2-dichlorobenzene). 2. An equal molar amount of tetramethylethylene (measured by ^{1}H NMR). 3. Ethylaluminum dichloride (usually 4 M in n-hexane) in a ratio of 1: 20 relative to the alkene. The reaction was slightly exothermic, and the temperature was maintained below 40 °C. After 10 min the reaction solution was shaken with enough triethylamine (twice as the molar amount of the catalyst) to quench the reaction and then 40 mL of water. The liquids decanted from the precipitate were then extracted with 50 mL of diethyl ether and concentrated under reduced pressure. The solution was dried over magnesium sulfate and fractionally distilled at 122 °C to afford 1.0 g (32%) of 1,1,2,2-tetramethyl-3-methylenecyclobutane. The ^{1}H and ^{13}C NMR spectra data were consistent with literature values.

Cycloadditions between Allene and Isopropylidenecyclohexane. The following compounds were consecutively dissolved in 20 mL of flurobenzene under nitrogen gas at 25 °C: 1.Allene to saturation *(ca.* 1 g, 25 mmol per 20 mL flurobenzene). 2. An equal molar amount of isopropylidenecyclohexane (measured by ^{1}H NMR). 3. Ethylaluminum dichloride (usually 4 M in n-hexane) in a ratio of 1: 20 relative to the alkene. The reaction was slightly exothermic, and the temperature was maintained below 40 °C. After 20 min the reaction solution was shaken with enough triethylamine (twice as the molar amount of the catalyst) to quench the reaction and then 40 mL of water. The liquids decanted from the precipitate were then extracted with 50 mL of diethyl ether and concentrated under reduced pressure. The solution was dried over magnesium sulfate and fractionally distilled to afford 1.40 g (46%) of the isomeric products, 1,1-dimethyl-3-methylenespiro[3.5]nonane (**3.5p1**) and 1,1-dimethyl-2-methylenespiro[3.5]nonane (**3.5p2**), at 195 °C. The products are characterized based on their C-C and C-H coupling constants on 2D NMRs (INADEQUATE and COSY) as shown in Figure 3.8.

NMR (δ (ppm), $CDCl_3$) of **3.5p1**: ^1H (500 MHz): 4.60 (d, J=2.2Hz, 1H), 4.55(td, J_1=1.5Hz, J_2=2.2Hz, 1H), 2.12 (m, 2H), 1.23-1.60 (m, 10H), 0.96 (s, 6H). ^{13}C (125 MHz): 156.1, 101.7, 47.4, 42.6, 36.4, 32.4, 23.6, 23.2, 22.8.

NMR (δ (ppm), $CDCl_3$) of **3.5p2**: ^1H (500 MHz): 4.79 (d, J=2.1Hz, 1H), 4.60(td, J_1=1.4Hz, J_2=2.1Hz, 1H), 2.19 (m, 2H), 1.22-1.62 (m, 10H), 1.03 (s, 6H). ^{13}C (125 MHz): 156.9, 104.3, 50.8, 40.5, 39.1, 32.3, 26.1, 23.7, 23.2.

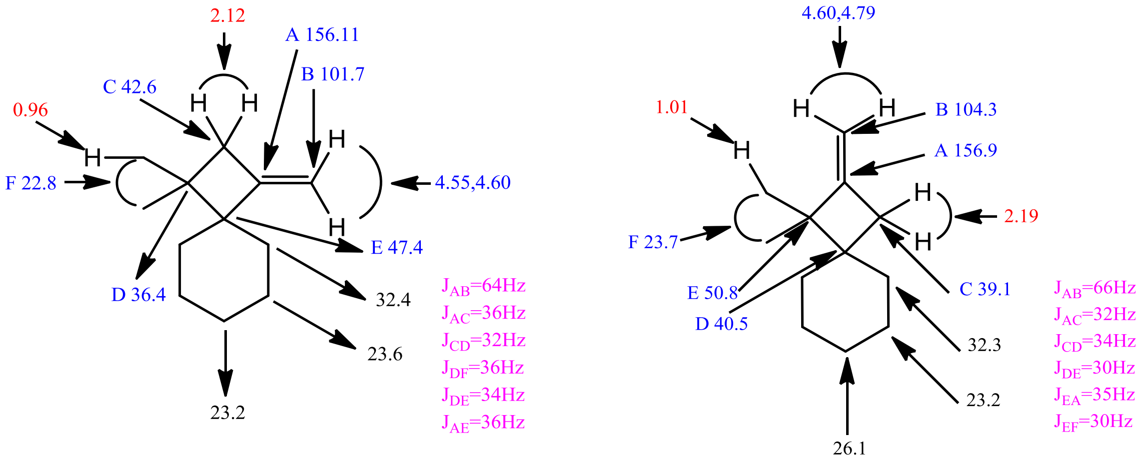


Figure 3.8. Product characterization by NMRs.

NMR Analysis of 1,1,2,2-Tetramethyl-3-methylenecyclobutane. All NMR samples consisted of 200 mg of the substrate in 5 mm NMR tubes filled to a constant height of 5 cm with C_6D_6. The ^{13}C spectra were recorded at 125.81 MHz using inverse gated decoupling, 120 s delays between calibrated $\pi/2$ pulses, and a 7 s acquisition time. Integrations were numerically determined using a constant integration region for each peak. A zero-order baseline correction was generally applied, but to avoid any qualitative manipulation no first-order or higher-order baseline correction was ever applied. Twelve spectra were recorded for each sample. The integration value of each peak was determined by the average of all measurements. The uncertainty of the measurement was determined by considering a two-side 95% confidence interval in a T-distribution.

Synthesis of Isopropylidenecyclohexane. This substrate was synthesized in three steps based on literature procedures[112] starting with cyclohexanone and isobutyl acid.

ISOTOPE EFFECTS AND THE MECHANISM OF THE STABILIZED WITTIG OLEFINATION

Introduction

The reactivity and selectivity of most organic reactions are governed by the geometries and energies of the transition states leading to the products. To obtain insight into the reactivity and selectivity of organic reactions, experimental studies have long sought to delineate qualitatively the structural features of the transition states, and computational studies have routinely focused on the quantitative properties of the transition state. The qualitative nature of experimental studies tends to limit the details of the resulting interpretations. Computational studies, in contrast provide specific and quantitative geometries for transition states, but the accuracy of the predictions is routinely unknown. In addition, diverse computational studies often make varied predictions for specific geometries of the transition states. Because of this, we have long sought to quantitatively define the geometries of transition states using a combination of experimental kinetic isotope effects (KIEs) and theoretical predictions of KIEs. The value of such process is that it provides experimentally based geometries that can serve to guide intuition. We consider that the application of this process to the Wittig olefination could be of particular value in order to aid in the understanding the stereochemistry of the reaction. Two important issues have arisen in the mechanistic studies of Wittig olefinations. The first is ordinary, the second is complex.

The traditional question arises, with regard to the Wittig olefination[113-114] mechanism, is to ask the nature of the intermediates along the reaction pathway and the identity of the rate limiting step (Figure 4.1). It was long thought that the olefination involves three steps. The first step is the formation of a zwitterion intermediate, as referred to betaine, the second step is the ring closure of the acyclic betaine to an oxaphosphetane, and the final step is the cleavage of the oxaphophetane to afford alkene and phosphorus oxide. This textbook mechanism has been strongly questioned in recent years due to diverse experimental and computational studies suggesting that the initial cycloaddition to afford the oxaphophetane is a concerted process and the intermediacy of the betaine is inconsistent with particular stereochemical observation in the reaction. The resulting mechanism favored in the literature then involves only two steps: a cycloaddition to afford the oxaphophetane and a retrocycloaddition to afford the final products. As being suggested, the first step is the rate limiting step for all salt free Wittig olefinations, although the direct evidence for this proposal is only qualitative for many forms of the reactions. Therefore, there remain interests to define unambiguously the nature of the rate limiting step in Wittig olefinations, particularly with stabilized ylides, as studied here.

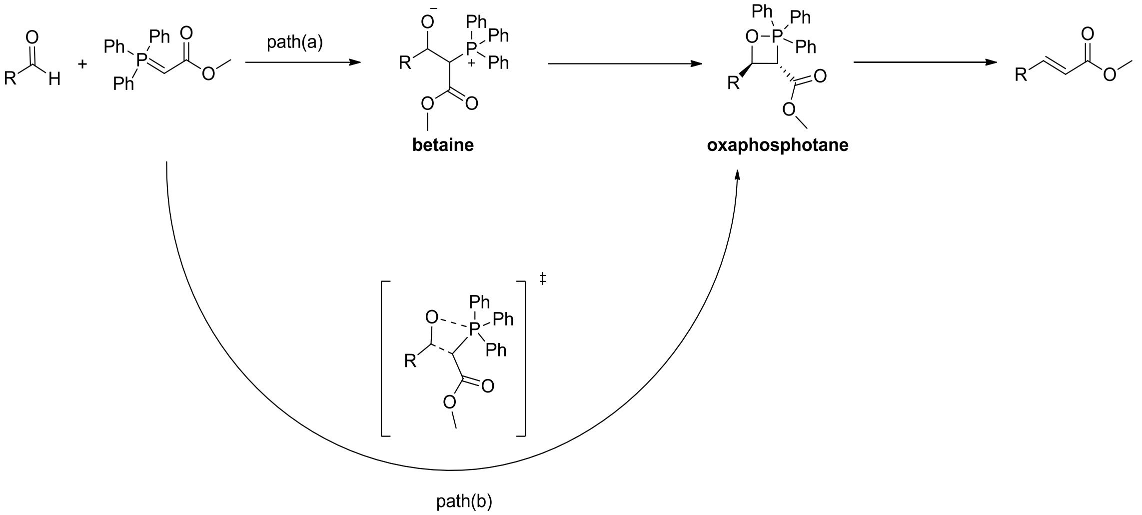
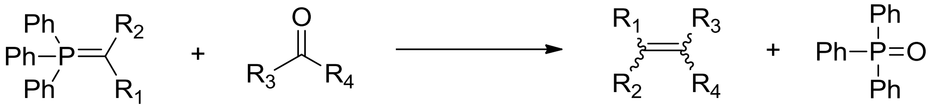


Figure 4.1. Two possible pathways for stabilized Wittig olefination: (a) Stepwise via betaine. (b) Asynchronous [2+2] cycloaddition.

A more complex question in this reaction is with regards to the dynamical nature of the cycloaddition. We have recently shown that in highly asynchronous cycloadditions, reactions have a tendency to exhibit dynamic effects, such as recrossing, that influence the experimental KIEs and stereochemistry of the reactions. The idea behind the special effect of dynamics on asynchronous cycloaddtions is that the first bond formation does not set up well the second bond formation. As a result, the first bond formation may reverse before the second bond formation occurs. By their non-pericyclic nature, the putative [2+2] cycloadditions involved in the formation of the oxaphosphetane would be qualitatively expected to be highly asynchronous and computational studies of Wittig reactions have supported this qualitative picture. It might then be envisioned that the carbon-carbon bond formation of the oxaphosphetane formation might not be accompanied dynamically by oxygen-phosphorus bond formation, even though the potential energy surfaces in these computational studies have involved a single barrier between the starting material and the oxaphosphetane. Another way to view this problem is to consider that after the carbon-carbon bond has completed in the cycloaddition, the oxygen atom of the original carbonyl and the phosphorus atom of the ylide are still far apart. While they are energetically attracted, their approach to form a bond could still involve an entropic barrier due to the restriction of vibrational bonds as the two atoms approach. Our previous studies have shown that an apparent concerted reaction can in fact act as and provide experimental observations that are indicative of stepwise cycloadditions. However we don't yet understand these dynamic effects well enough to be able to predict which cycloaddition will be influenced by dynamic effects and which will not. In the Wittig reaction, one might envision that conformation of the P-O bond formation will be governed by the balance between the energetic attraction of the oxygen and the phosphorous atoms in the short time after the transition state, versus the entropic cost of forming a bond between the two atoms. If the O and P is strongly bond, it might then be expected that they form bond shortly after the transition state and now dynamic effect will be involved. It was in fact our expectation, but the limited stage of the knowledge in this area made it important for us to evaluate this question experimentally.

Wittig olefination is very useful in stereospecifically introducing C=C double bonds. This transformation combines carbonyl compounds, usually aldehydes or ketones, with phosphoranes (phosphorous ylides) to afford the corresponding olefins. The stereoselectivity of the reaction is generally determined by the type of ylides. Stabilized ylides, which have strong electron withdrawing substituents, i.e. ester groups, on the carbon, gives high E selectivity. Non-stabilized ylides, which has electron donating substituents, i.e. alkyl groups, gives high Z selectivity. Semi-stabilized ylides, which has moderate electron withdrawing substituents, i.e. aryl groups, gives poor stereoselectivity. Despite debates over the detailsin specific reaction substrates or conditions, a commonly accepted reaction mechanism involves an initial C-C bond formation between the carbonyl carbon and the negative charged carbon in the phosphorous ylide, and a following oxaphosphetane (OP) intermediate that leads to the olefin product. Previous studies have shown that the stereoselectivity of the reaction is affected by many factors such as the type of ylides, the polarity of the solvents, and the ions in the solutions. But more importantly, the transition state geometry is believed to account for the stereo outcome of Wittig olefinations.

The mechanistic study of Wittig olefination was stimulated by many of its unusual observations, i.e. high Z selectivity in the reaction using non-stabilized ylides. Despite of many debates and confusions early on, it was soon well established that this reaction has two major steps: the formation of the oxaphosphetane intermediate from the starting materials and the decomposition of the oxaphophetane to afford the final alkene product. The studies then moved on mainly to address two important issues in the mechanism. The first issue resides in the formation of the oxaphosphetane that is whether the betaine is an intermediate or not in this process. The second issue resides in the decomposition of the oxaphosphetane that is why different types of ylides have different stereo control in this reaction (Figure 4.2).



R_1=R_2=**H,alkyl**	non-stablized ylide	Z-selective
R_1 or R_2=**aryl**	semi-stablized ylide	non-selective
R_1 or R_2=**carbonyl**	stablized ylide	E-selective

Figure 4.2. Three types of Wittig olefinations.

Shortly after the Wittig olefination was published, the betaine was proposed to be the only intermediate in this reaction, whereas the oxaphosphetane was mostly believed to be a transition state at that time. This postulation was supported by various experimental observations[115-116] as shown in figure 4.3: 1.the formation of lithium betaine adduct and subsequent amplification of the Z selectivity when lithium halide salt was added under reaction conditions. 2. The trapping of betaine as β-hydroxy phosponium salts when acid was added to the reaction at low temperature. However, this postulation did not stand long in front of the test of time.

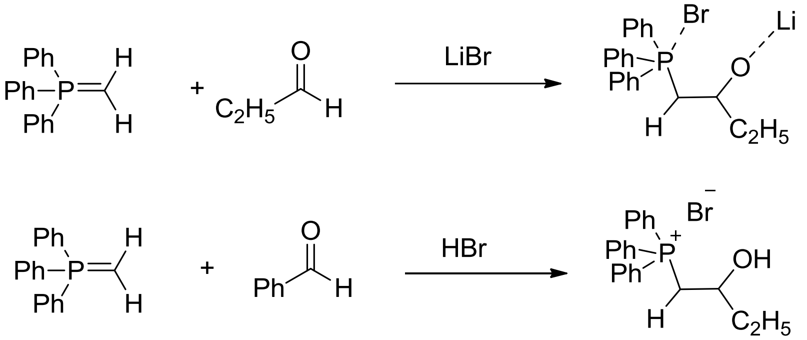


Figure 4.3. Experimental observations for betaine being an intermediate.

In 1980s, a series of important discoveries were made to refine the mechanism of Wittig olefinations. Firstly, oxaphosphetane was solely observed experimentally by Vedejs using ^{31}P NMR in reaction between non-stabilized ylides and aldehydes.[117] The observed ^{31}P chemical shifts (-50 ppm to -70 ppm) in many reactions are characteristic for a pentavalent phosphorous compound (oxaphosphetane), and no ^{31}P (+30 ppm to +50 ppm) were observed for tetravalent phosphorous compounds(betaine).Secondly, the oxaphosphetane intermediate was successfully separated and characterized from non-stabilized Wittig olefinations using dibenzolphosphole (DBP) derived ylides.[118] The stability of the oxaphosphetane was believed to relate to the pseudo-rotation of the penta-valent phosphorus. If the pseudorotation around the phosphorous is restricted, as shown in the DBP derived ylides, the resulting oxaphosphetane is much more robust than ordinary ones. Further studies of the oxaphostante showed that when subjected to lithium halide salts or acids, it could also form the corresponding betaine adduct/ β-hydroxy phosponium salts. These observations means that the previously observed betaine adduct/ β-hydroxy phosponium salts could originate from the oxaphosphetane intermediate, instead of the reaction condition. All these observations established the intermediacy of oxaphosphetane in non-stabilized Wittig olefinations, and at the same time put the intermediacy of betaine under question, because no direct observations of the betaine were documented under any reaction conditions.

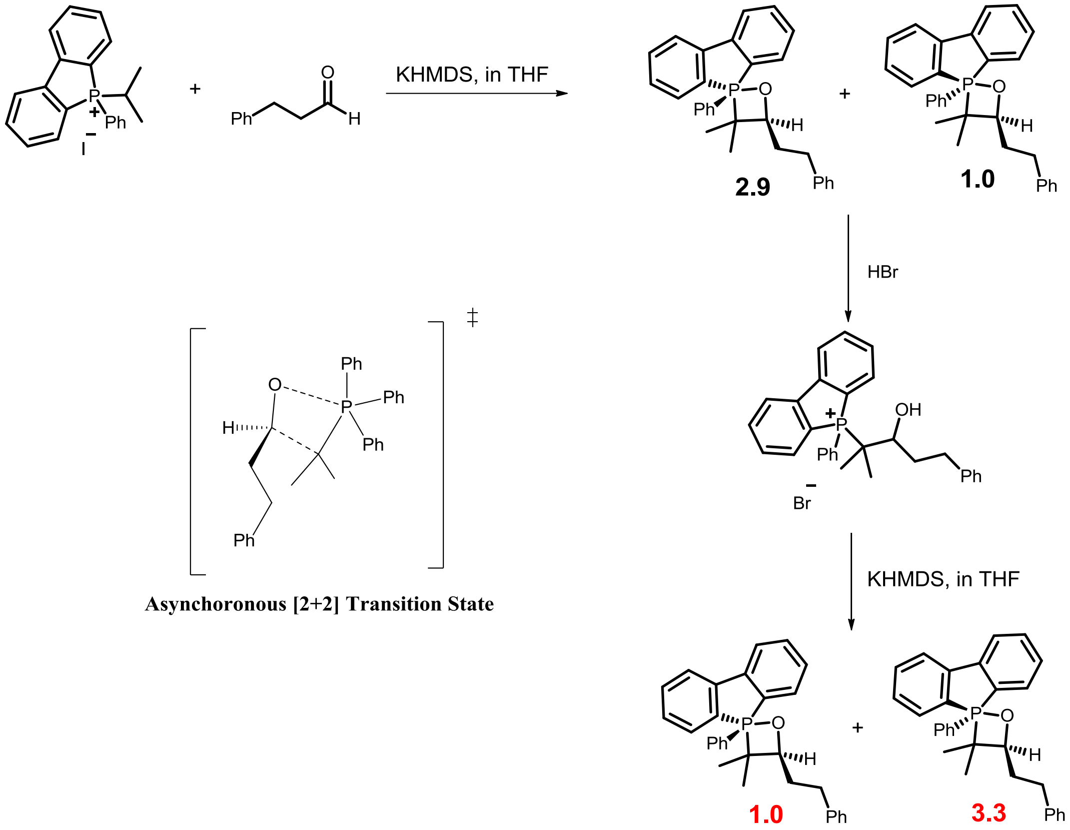
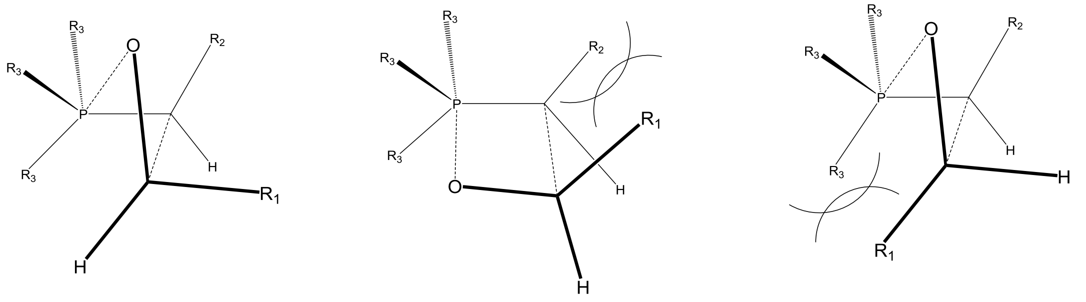


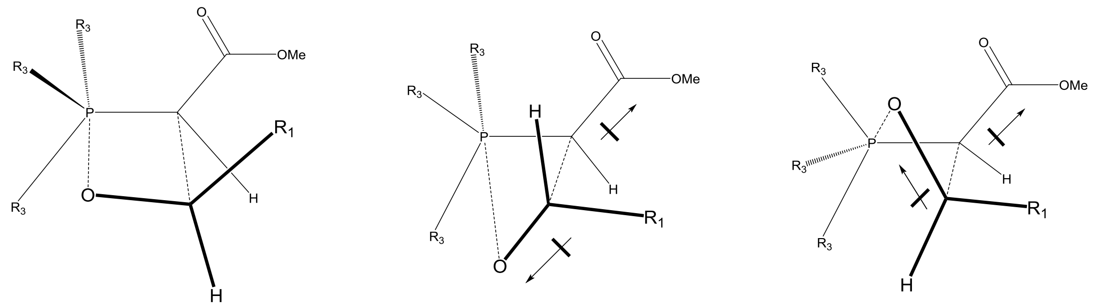
Figure 4.4. Experimental observations for oxaphohsphetane being intermediate and asynchoronous [2+2] cycloaddition transition state.

In 1990, Vedejs published a compelling experiment result by comparing the stereo outcomes from the Wittig olefination and the corresponding betaine decomposition, to rule out the possibility of betaine formation in the non-stabilized Wittig olefination[119] (Figure 4.4). The result showed that the two reactions afforded the same oxaphosphetane intermediates, but in a very different ratio. This result strongly supported the [2+2] cycloaddition pathway and disfavored the betaine intermediate, at least within the time scale of C-C bond rotation in the non-stabilized Wittig olefination. Based on these experimental evidences, an asynchronous [2+2] cycloaddition was proposed to account for the formation of oxaphosphetane, leaving the betaine out of the mechanistic picture.

Computational studies supported this proposal. Various ab initial and DFT methods with small basis sets, i.e. 6-31G* depicted the energy surface of the formation of oxaphosphetane as a single step.[120-123] The betaine was found not to be a local minimum on the energy surface. This asynchronous [2+2] cycloaddition step was also believed to be the origin of the stereo control in Wittig olefinations. Different transition state structures of the cycloadditions were proposed for different type of ylides, and they lead to different stereo outcome of the reactions.[124-125] Vedejs proposed a transition state model in 1989 to explain the stereoselectivity in Wittig olefination.[126] In this model, the transition structure conformation depends on the type of the yilde. In a stabilized Wittig olefination, the transition structure adapted a staggered conformation that allows the substituent on the aldehyde to be anti to the ester group, but gauche to the triphenylphosphine. In a non-stabilized Wittig olefination, the transition structure will prefer the conformation that allows the substituent on the aldehyde to be anti to the triphenylphosphine, but gauche to the alkyl group. This difference qualitatively accounts for the different stereoselectivities. In 2006, Robiette et al proposed a different transition state conformation for stabilized Wittig olefinations.[127-128] In this proposal, the transition structure prefers a conformation that allows the substituent on the aldehyde to be anti to the triphenylphosphine group, while the oxygen is anti to the ester group. This conformation is favored due to a dipole-dipole interaction between the carbonyl group and the ester group (Figure 4.5).



(a) cis-puckered TS(favored) **(b) cis-planar TS(disfavored)** **(c) trans-puckered TS(disfavored)**



(d) cis-planar TS(disfavored) **(e)trans-slightly puckered TS(favored)** **(f) cis-slightly puckered TS(disfavored)**

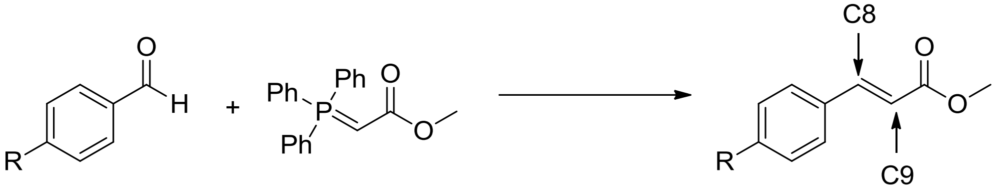
Figure 4.5. Proposed transition structure for different types of Wittig olefinations and the corresponding selectivity: (a)-(c): non-stabilized ylides. (d)-(f): stabilized-ylides.

In the light of numerous literature precedence, the mechanism of non-stabilized Wittig olefination seemed to be well resolved. As for the reactions with stabilized ylides, due to the limitation of experimental observations, the current understanding of the mechanism in stabilized Wittig olefination is mainly based on the corresponding observations from the non-stabilized counterparts and computational modelings. In 2012, Gilheany generalized the mechanism to semi and stabilized Wittig olefinations[129] based on the experimental observation that reactions with β-heteroatom-substituted aldehydes are consistently selective for cis-oxaphosphetane-derived products. The author concluded that the stereoselectivity of all Wittig reactions is explicable by the single mechanism, especially stabilized ylide cases. Although all Wittig olefination reactions share some common feature in their mechanisms, it is not safe to assume that all types of Wittig olefinations undergo the same type of mechanism.

We describe here a combined experimental and computational study of the prototypical Wittig reaction of the stabilized ylide, methyl triphenylphosphoranylidene acetate, with benzyl aldhyde. The patten of ^{13}C KIEs observed in this reaction is consistent with a cycloaddition for the oxaphophetane, and is inconsistent with any significant contribution from rate limiting breakdown of the oxaphophetane. Computational studies are found to predict diverse geometries for the transition states of oxaphophetane formation, and the experimental KIEs allow the distinction between these geometries. A dynamic study of the oxaphosphetante formation illustrates the unusual trajectories associated with betaine formation and recrossing. The reaction mechanism is better described as a two-step process instead of concerted one in the formation of oxaphosphetane. Overall, the results provide detailed insight into the intermediacy of the betaine in the stabilized Wittig olefination based on experimental KIEs and theoretical predictions.

Results

Experimental KIEs. Three substances, benzaldehyde, p-methoxy and p-nitro benzaldehyde, were reacted with methyl triphenylphosphoranylidene acetate respectively to afford the corresponding olefins. This experimental design requires two reactions for each substance, one reaction taking the aldehyde to low conversion (~20%) and the methyl triphenylphosphoranylidene acetate to 100% conversion, the other one is vice versa. The low-conversion reaction for one of the starting materials serves as the 100% reaction standard for the other starting material. The ^{13}C KIEs were determined by NMR analysis at natural abundance. The results are summarized in figure 4.6.



R	**KIEs on C8 and C9**
OMe	1.037, 1.012
H	1.040, 1.014
NO_2	1.041, 1.015

Figure 4.6. Experimental product KIEs for three different substrates.

All three reactions exhibit significant KIEs at C8 and C9, which fits qualitatively to the hypothesis that C8 and C9 undergoes bond changes the rate limiting transition state. The experimental KIEs is consistent with the formation of the oxaphosphetane being rate limiting, and inconsistent with any substantial contributions to the rate limiting step from the breakdown of the oxaphosphetane. The trends of the KIEs on C8 notably suggest that the transition state goes late from p-nitro benzyl aldehyde to benzyl aldehyde, to *p*-methoxy benzaldehyde. A quick explanation for this trend is the electronics of the aldehydes. *p*-Nitro benzyl aldehyde is the most electron deficient aldehyde and thus is most reactive, resulting in an earlier transition state than the most electron rich aldehyde, which is the *p*-Methoxy benzaldehyde. However, the experimental KIEs itself does not distinguish path (a) from path (b) in the formation of the oxaphosphetane. In order to better illustrate the reaction mechanism, we have to consider transition state theory and dynamic effects.

Theoretical Predictions. Transition state theory has been widely and successfully applied in predicting and rationalizing the selectivity and reactivity of common organic reactions. However, it is very difficult to directly observe transition state geometries using common experimental techniques. Thus, transition structures of organic reactions are mainly understood based on theoretical modeling. Based on our previous studies, experimental kinetic isotope effects (KIEs) can serve as an excellent measure of the theoretical prediction. Despite expected limitations, a close correspondence between predicted and experimental KIEs has been observed in many cases, and this has been interpreted as supporting the accuracy of the calculated transition structures.

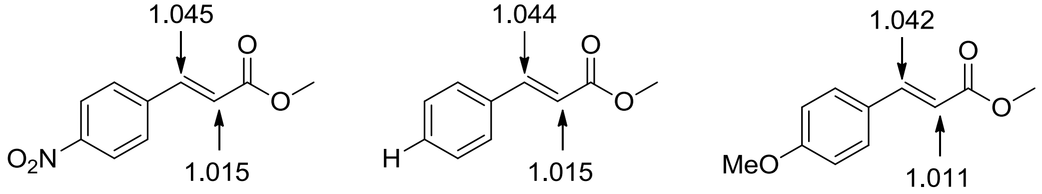


Figure 4.7. Calculated product KIEs for three different substrates using B3LYP/6-31G* with implicit PCM solvent model for tetrahydrofuran.

Theoretical calculations presented in figure 4.7 predict the KIEs in a qualitative agreement with experimental values. However, the experimental values on C8 are systematically lower than theoretical predictions. This observation is seen both in our experiments and literature precedencies. Although the difference is small, it indicates intrinsic complexity in the reaction mechanism.

To address this issue, we choose to study the reaction between p-methoxy benzaldehyde and 1-(triphenylphosphoranylidene)-2-propanone, presumably because this reaction gives more recrossing. The experimental KIEs are shown in figure 4.8.

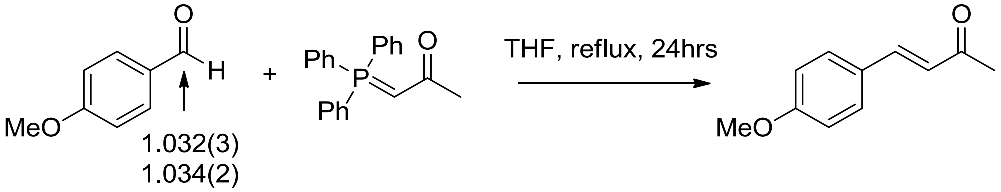


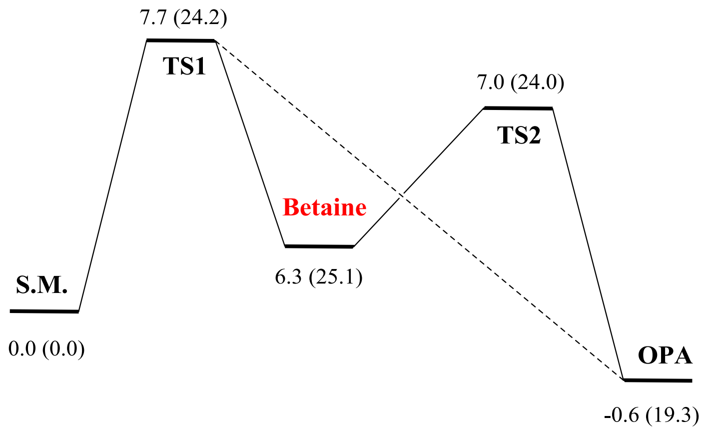
Figure 4.8. Experimental KIEs for p-methoxy benzaldehyde.

In this case, the experimental KIEs were even lower than what theory predicts-1.043. This discrepancy can not be understood by the modern understanding of the reaction mechanism. Based on a concerted asynchronous transition state, the KIEs are much higher than experimental values and thus we need to reconsider the mechanism of this reaction.

Discussion

From the perspective of conventional transition state theory, the smaller experimental KIEs compared to what theory predicts suggest that the initial C-C bond formation is not fully rate-limiting. Based on the reaction energetics, the decomposition of the oxaphosphetane is much lower in energy compare to the initial transition state, so that only leave us with one choice-the P-O bond formation is partially rate limiting in this reaction, which means there is a betaine intermediate in this reaction.

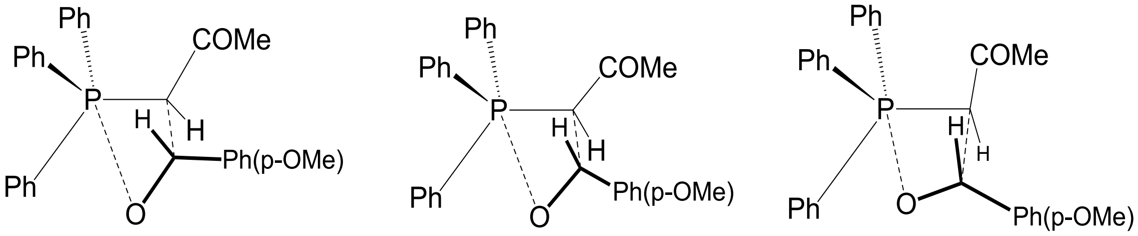
Theoretical calculations were performed to verify this idea. When using M062X/6-31+G** with a continuum solvent model for THF, the betaine intermediate was located as a potential energy minimum, which was not well recognized before. One reason for not locating the betaine intermediate computationally is the choice of basis set: a relative small basis set, i.e. 6-31G*, does not have the diffusion function on the negatively charged oxygen atom and will underestimate the stability of this zwitter ionic intermediate. Due to the relative big size of the system and the limited computational power, it was very common for early researchers to only apply small basis sets or use over-simplified system to model this reaction. Our choice of method and basis set defines the energy surface of this reaction in a more accurate way (Figure 4.9). The formation of the oxaphosphetane (**OPA**) undergoes a two-step process involving a zwitter ionic intermediate (**Betaine**). The first step (**TS1**) is mainly C-C bond formation between the ylide carbon and the carbonyl carbon. The betaine intermediate then does a pseudo rotation around the phosphorous atom to form the second P-O bond (**TS2**).



M06-2X/6-31+G(d,p) pcm model for THF, potential energy(free energy) kcal/mol

Figure 4.9. Energy profile of Wittig olefination between p-methoxy benzaldehyde and 1-(triphenylphosphoranylidene)-2-propanone.

A careful examination of the transition structures revealed more details about the mechanism. First of all, **TS1**, **Betaine** and **TS2** all adapt similar but a tighter conformations to previously proposed structures, with a key difference in the bonding C-C and P-O distances. This allows and increases the importance of steric interactions at the transition states. Second, at **TS1**, the C-C bond is 1.89 Å while the P-O is still 3.1 Å, this indicates that an asynchronous [2+2] cycloaddition is not feasible simply because P-O is too far to have any meaning for orbital interactions. The force that holds P and O close is mainly electronic statics. As the C-C bond is forming, the O-P distance decreases to a potential energy minimum (2.53 Å in betaine). A second barrier (**TS2**) prevents an instantaneous O-P bond formation presumably due to the steric interaction between the phenyl substituent and the oxygen. As the reaction proceeds from **TS1** to **Betaine** to **TS2**, the structure is tighter and more planar (Figure 4.10).



TS1
C-C: 1.89
P-O: 3.14
PCCO: 52.37

Betaine
C-C: 1.64
P-O: 2.91
PCCO: 50.52

TS2
C-C: 1.59
P-O: 2.53
PCCO: 40.13

Figure 4.10. Transition strucutures and intermediates of Wittig olefination between p-methoxy benzaldehyde and 1-(triphenylphosphoranylidene)-2-propanone.

Based on conventional transition state theory prediction, TS1 has a KIE of 1.043 and TS2 has a KIE of 1.015. Since these two transition states are very close in energy, they should both contribute to the final KIE of the reaction. The experimental KIE of 1.033 is in good agreement with this model and thus support the idea that the formation of oxaphosphetane is a two-step process.

From the perspective of variational transition state theory, this observation also indicates recrossing at the transition state. The variational transition state theory improves transition state theory by taking entropy into consideration. When using variational transition state theory, the position of the transition state between reactant and product regions is optimized to minimize the reaction rate. This addresses the effects of recrossing on the potential energy surface because it generally put the variational transition state later than the conventional transition state. So the KIEs prediction based on variational transition state theory tends to be lower than those from conventional transition state theory. To locate the variational transition state, polyrate calculations were performed. The resulting structure indeed gave a good prediction on the experimental KIEs. The shortcoming of this method is that it is purely statistical, leaving out the details of dynamic effects in this reaction.

Another approach is to do trajectory simulations. Quassi-classical trajectories were performed from the transition state and led to three possible outcomes. The first outcome is recrossing. Over 50% of the trajectories went back to the starting material before the P-O bond formed. These trajectories took around 100 fs to do this and could result in decreased KIEs. The second outcome is the formation of betaine intermediate. 40% of the trajectories afforded the betaine intermediate, not the oxaphosphetane. The time that the trajectories stayed in the betaine state is around 200 fs. This result is consistent with the intermediacy of betaine and provides another aspect to interpret the decreased KIE. As an intermediate, the betaine is in equilibrium with the reactants. This equilibrium will affect the distributions of isotopomers in the final products and re-isolated starting materials, which will be reflected as decreased KIEs. There have been experimental evidences of the decomposition of in-situ generated betaines to the reactants. Various experimental and theoretical evidence have shown that the intermediacy of betaine is not necessary in non-stabilized Wittig olefinations, but our trajectories showed the opposite in the stabilized case. The third outcome is the formation of the oxaphosphetane, which is very minor (<5%). The direct formation of the oxaphosphetane is not a plausible process based on the trajectory simulations. This again is against the idea that the formation of oxaphosphetane does not involve the betaine intermediate. The advantage of trajectory simulation is that it takes both statistical and non-statistical recrossings into consideration; the disadvantage is that it takes longer time for an accurate prediction.

Another interesting observation from trajectory simulations is that the recrossing seems to have an effect on the stereo selectivity of the reaction. As literature reported, Wittig olefination between stabilized ylides and aldehydes has a high E selectivity for the product, but the transition state theory can not explain the selectivity quantitatively. When we perform trajectory simulations from the transition states for Z and E products, we found out trajectories starting from the Z transition state recross much more than the trajectories from the E transition state. This trajectory simulation, together with the traditional transition state theory predictions, explains the stereoselectivity very well.

Conclusion

Previous studies have generalized a unified [2+2] cycloaddition mechanism for oxaphosphetane formation in all types of Wittig olefinations. However, the experimental evidence for this generalization neglect the fact the similarity between [2+2] cycloaddition transition state from starting materials and the ring closure transition state from betaine. Computational results were not convincing due to the imperfect choice of the methods and basis set, which underestimated the stability of the betaine intermediate.

Based on our study of stabilized Wittig olefination, a stepwise mechanism of the formation of oxaphosphetane is supported. Both experimental observations and theoretical calculations were consistent with the intermediacy of the betaine. Moreover, the trajectory studies also showed the reaction has a betaine intermediate and significant recrossing at the transition state. The outcome of trajectory simulations was in agreement with experimental KIEs and stereoselectivities. To fully understand the experimental KIEs, we used both conventional transition state theory and variational transition state theory to predict the KIEs.

In conclusion, Wittig olefination between aldehydes and stabilized ylides does not undergo an asynchronous [2+2] cycloaddition to form the oxaphosphetane. Instead, the reaction proceeds in a two-step process involving a transparent betaine intermediate. The stepwise mechanism gives good predictions on the experimental KIEs and involves significant transition state recrossing.

Experimental Section

General Procedure. All aldehydes and ylides were purchased from Aldrich and used without further purification unless otherwise specified. All glassware were oven dried at 200 ºC before use. Tetrahydrofuran (THF) was freshly distilled from sodium/benzophenone before use. All chromatography were performed using silica gel (40-60 μm) under positive N_2 pressure. NMR spectra were recorded on modern 500 MHz Varian spectrometers at ambient probe temperatures unless otherwise stated. Chemical shifts were referenced to internal residual signal of $CHCl_3$ (^1H, δ=7.26 ppm) and $^{13}CDCl_3$ (^{13}C, δ=77.1 ppm).

Wittig Reaction between Benzaldehyde and Methyl (triphenylphosphoranylidene)Acetate. Methyl (triphenylphosphoranylidene)acetate (3.34 g, 10 mmol, 1 equiv) was dissolved in 50 mL of THF. Benzaldehyde (5.30 g, 50 mmol, 5 equiv) was then added to the solution. The reaction mixture was stirred at room temperature for 24 h. NMR analysis of an aliquot taken from the reaction mixture showed quantitative conversion of the ylide. The solution was then concentrated in vacuo and 100 mL of pentane was added to precipitate out the triphenylphosphine oxide. After filtration, the solvent was removed under reduced pressure. The residue was chromatographed on a 10"× 36 mm silica gel column using 20% ethyl acetate in hexanes as eluent to afford 1.02

g (63%) of methyl (2*E*)-3-phenyl-2-propenoate (>98% pure; with impurities of the corresponding *Z* isomer). The ^{1}H and ^{13}C NMR spectrum data of the material were consistent with literature values.[130]

An analogous reacion was carried out by an identical procedure using methyl (triphenylphosphoranylidene)acetate (16.7 g, 50 mmol, 5 equiv) and benzaldehyde (1.06 g, 10 mmol).

Wittig Reaction between *p*-Anisaldehyde and Methyl (triphenylphosphoranylidene)Acetate. Methyl (triphenylphosphoranylidene)acetate (3.34 g, 10 mmol) was dissolved in 50 mL of THF. *p*-Anisaldehyde (6.80 g, 50 mmol, 5 equiv) was then added to the solution. The reaction mixture was stirred at room temperature for 24 h. NMR analysis of an aliquot taken from the reaction mixture showed quantitative conversion of the ylide. The solution was then concentrated in vacuo and 100 mL of pentane was added to precipitate out the triphenylphosphine oxide. After filtration, the solvent was removed under reduced pressure. The residue was chromatographed on a 10"× 36 mm silica gel column using 20% ethyl acetate in hexanes as eluent to afford 1.23 g (64%) of methyl (2*E*)-3-(4-methoxyphenyl) acrylate (>98% pure; with impurities of the corresponding *Z* isomer). The ^{1}H and ^{13}C NMR spectrum data of the material were consistent with literature values.[130]

An analogous reaction was carried out in an identical procedure using methyl (triphenylphosphoranylidene)acetate (16.7 g, 50 mmol, 5 equiv) and *p*-anisaldehyde (1.36 g, 10 mmol).

Wittig Reaction between 4-Nitrobenzaldehyde and Methyl (triphenylphosphoranylidene)Acetate. Methyl (triphenylphosphoranylidene)acetate (3.34 g, 10 mmol) was dissolved in 50 mL of THF. 4-Nitrobenzaldehyde (7.55 g, 50 mmol, 5 equiv) was then added to the solution. The reaction mixture was covered with aluminum foil and stirred in dark at room temperature for 24 h. NMR analysis of an aliquot taken from the reaction mixture showed quantitative conversion of the ylide. The solution was then concentrated in vacuo and 100 mL of pentane was added to precipitate out the triphenylphosphine oxide. After filtration, the solvent was removed under reduced pressure. The residue was chromatographed on a 10"× 36 mm silica gel column using 20% ethyl acetate in hexanes as eluent to afford 1.45 g (70%) of methyl (2*E*)-3-(4-nitro) acrylate (>98% pure; with impurities of the corresponding *Z* isomer). The ^{1}H and ^{13}C NMR spectrum data of the material were consistent with literature values.[130]

An analogous reaction was carried out in an identical procedure using methyl (triphenylphosphoranylidene)acetate (16.7 g, 50 mmol, 5 equiv) and 4-nitrobenzaldehyde (1.51 g, 10 mmol).

NMR Analyses of Methyl (2*E*)-3-phenyl-2-Propenoate, Methyl (*E*)-3-(4-methoxyphenyl)Acrylate and Methyl (*E*)-3-(4-nitro)Acrylate. All NMR samples consisted of 300 mg of the products in 5 mm NMR tubes filled to a constant height of 5 cm with $CDCl_3$. The ^{13}C spectra were recorded at 125.81 MHz using inverse gated decoupling, a $5*T_1$ delay between calibrated $\pi/2$ pulses, and a 7 s acquisition time, defining T_1 as the longest relaxation time of all the ^{13}C signals in the sample. The T_1 values for methyl (2*E*)-3-phenyl-2-propenoate, methyl (*E*)-3-(4-methoxyphenyl) acrylate and methyl (*E*)-3-(4-nitro) acrylate were 14 s, 17 s, and 22 s respectively, based on the peaks at 134.4 ppm, 127.1 ppm and 142 ppm respectively. Integrations were numerically determined using a constant integration region for each peak. A zero-order baseline correction was generally applied, but to avoid any qualitative manipulation no first-order or higher-order baseline correction was ever applied. At least six spectra were recorded for each sample. The integration value of each peak was determined by the average of all measurements. The uncertainty of the measurement was determined by considering a two-side 95% confidence interval in a T-distribution.

Wittig Reaction between *p*-Anisaldehyde and 1-(triphenylphosphoranylidene)-2-Propanone. To 150 mL of THF were added consecutively 1-(triphenylphosphoranylidene)-2-propanone (25.47 g, 80 mmol) and *p*-anisaldehyde (13.6 g, 100 mmol). The reaction mixture was stirred under reflux for 24 h. NMR analysis of an aliquot taken from the reaction mixture showed 69% conversion of the *p*-anisaldehyde. The solution was then concentrated in vacuo and 200 mL of pentane was added to precipitate out the triphenylphosphine oxide. After filtration, the solvent was removed under reduced pressure. The residue was chromatographed on a 12"× 60 mm silica gel column using 20% ethyl acetate in hexanes as eluent to afford 1.01 g (37.1%) of unreacted *p*-anisaldehyde (>99% pure, with impurities of (*Z*)-4-(4-methoxyphenyl)but-3-en-2-one). The ^{1}H and ^{13}C NMR spectrum data of the material matched with those of an authentic sample.

An independent reaction was taken to 73% conversion following a closely analogous procedure.

NMR Analyses of *p*-Anisaldehyde. All NMR samples consisted of 300 mg of the substrate in 5 mm NMR tubes filled to a constant height of 5 cm with $CDCl_3$. The ^{13}C spectra were recorded at 125.81 MHz using inverse gated decoupling, 70 s delays between calibrated $\pi/2$ pulses, and a 5 s acquisition time. The 70 s delay was based on the T_1 of the signal at 130 ppm, which was measured to be 14 s. Integrations were numerically determined using a constant integration region for each peak. A zero-order baseline correction was generally applied, but to avoid any qualitative manipulation no first-order or higher-order baseline correction was ever applied. At least six spectra were recorded for each sample. The integration value of each peak was determined by the average of all measurements. The uncertainty of the measurement was determined by considering a two-side 95% confidence interval in a T-distribution.

DYNAMICALLY COMPLEX ENZYME-CATALYZED [6+4] AND [4+2] CYCLOADDITIONS IN THE BIOSYNTHESIS OF SPINOSYN A

Introduction

The prominence of the Diels-Alder reaction in synthetic chemistry has led to extensive interest in its role in biosynthetic pathways. The known secondary metabolites include hundreds of structures for which an enzyme-catalyzed Diels-Alder reaction could plausibly be involved in the biosynthesis, but the existence of "Diels-Alderases" has been supported for only a small handful of structures. The strongest evidence for a stand-alone Diels-Alderase has recently been presented for SpnF, an enzyme that catalyzes a key transannular Diels-Alder reaction in the biosynthesis of spinosyn A. As historically defined, the Diels-Alder reaction of a 1,3-diene and an alkene must afford the cyclohexene product in a single mechanistic step, that is, by a concerted pericyclic transition state, and this requirement has been used to dismiss proposed Diels-Alderases that catalyze stepwise cycloaddition mechanisms. This mechanistic definition of the Diels-Alder reaction does not take into account a number of complications in the mechanism of cycloadditions that have come to light in recent years, particularly with regard to dynamic effects on the rate and selectivity. We describe here the importance of such complications in the transannular Diels-Alder reaction catalyzed by SpnF, including the role of a [6+4] cycloaddition, a bispericyclic transition state, a bifurcating energy surface, a dynamically stepwise cycloaddition, an entropically-delineated intermediate, and transition state recrossing in the mechanism. The underlying cycloaddition that is catalyzed by SpnF is not its caricature from classical mechanistic analysis and it is not well described by either concerted or stepwise labels. Instead, the mechanism is richer and can only be understood by consideration of dynamics. The significance of this work lies in its expansion of the ideas that must be employed to understand the mechanistic nature of reactions catalyzed by enzymes and the potential role of enzymes in controlling reactions.

Spinosyn A is a natural product of *Saccharopolyspora spinosa* that is the principle component in the broad-spectrum commercial insecticide Spinosad.[130] The functions of most of the enzymes (SpnA - SpnS) encoded by the spinosyn biosynthetic gene cluster have been determined, and the biosynthesis of the unique tetracyclic core of spinosyn A appears to follow an ordinary polyketide synthase-mediated pathway up to the formation of the monocyclic keto-intermediate **1** (Figure 5.1)**.**[131] Liu and coworkers found that the treatment of **1** with SpnM led to the formation of the tricyclic **3**, and they observed the transient monocyclic dienone intermediate **2**. SpnM was found to catalyze the dehydration forming **2** but not the cyclization of **2** to **3**. Instead, this cyclization occurs spontaneously, though slowly, and a different enzyme, SpnF, was found to catalyze this [4+2] cycloaddition.[132] The description of a reaction as a cycloaddition carries no mechanistic implication, but its designation as a Diels-Alder reaction has been limited to reactions that do not involve intermediates.[133-134] As a result, the question of whether SpnF is a 'Diels-Alderase'[135-137] would conventionally focus on the mechanism of the cycloaddition and whether it occurs by a concerted process. We have studied this mechanism using theoretical calculations.

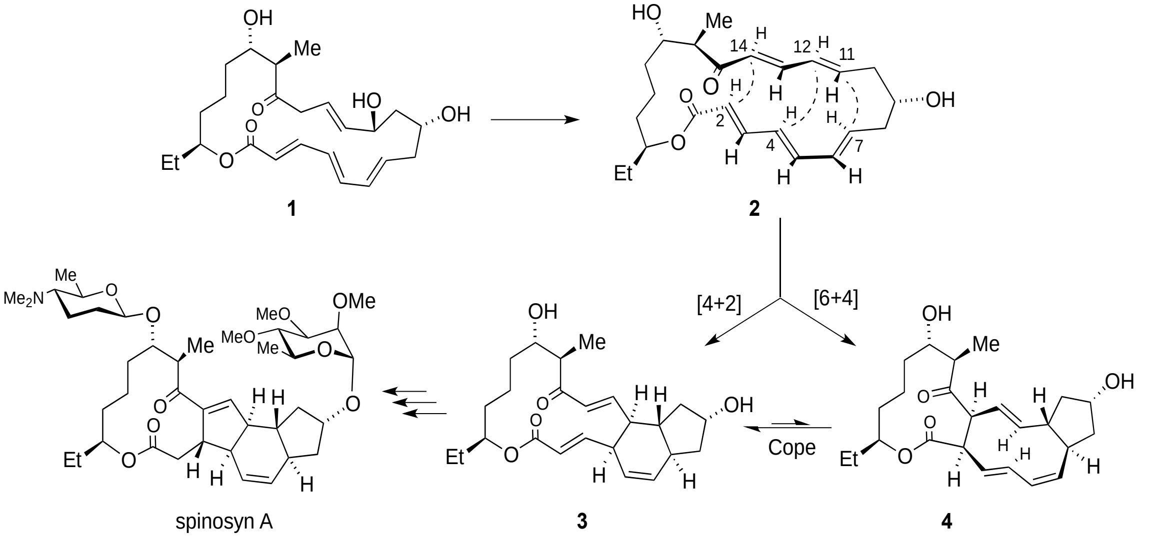


Figure 5.1. The cycloaddition in the spinosyn biosynthesis. The bispericyclic transition state for the cycloaddition of **2** affords both **3** and **4**.

Results

The study of the cyclization of **2** to **3** is complicated by the ensemble of conformations that are energetically available to **2** as well as the potential for alternative modes of approach of the cycloaddition addends that could lead to stereoisomers of **3**. A conformational search of the ground state of **2** was undertaken using an MMFF force field and the low mode / Monte Carlo search protocol optimized for sampling of macrocycles available in Macromodel 9.9. Transition structure conformations for each possible cycloaddition mode were obtained by simulated annealing of structures in which the C^4-C^{12} and C^7-C^{11} distances were fixed at values typical of Diels-Alder reactions. Simulated annealing was also used to obtain conformations for the possible cycloadducts. The twenty to thirty lowest-energy structures in each case were then used as the starting points for full optimizations in DFT calculations. Geometry optimizations were conducted using B3LYP calculations including Grimme's empirical D2 correction and using a 6-31G(d) basis set. B3LYP/def2-TVZPP//B3LYP-D2/6-31G(d) and M06-2X/def2-TVZPP//def2-TVZPP//B3LYP-D2/6-31G(d) single-point calculations were used to gain more accurate estimates for reaction energetics. Additional single-point calculations were carried out using SMD and CPCM solvation models for water and ether, but the results suggest that neither solvent has a substantial effect on the absolute or relative barrier heights. The discussion here will present the gas-phase energetics (Figure 5.2).

Remarkably, none of the low-energy transition structures are those of simple Diels-Alder reactions. Instead, the lowest-energy transition structure **5**‡ (Figure 5.3) as well as the other low-energy structures are *bispericyclic.*[138] A bispericyclic transition state is one that is stabilized by two sets of cyclic aromatic orbital interactions, with each set corresponding to a distinct mode of cycloaddition. The known bispericyclic transition states involve Diels-Alder reactions in which each addend may function as either the four-electron (diene) or two-electron (dienophile) component in the reaction, allowing the transition state to simultaneously have both [4+2] and [2+4] character.[139-143] The energy surface following a bispericyclic transition state is *bifurcating* in that downhill paths can lead to two or more products.

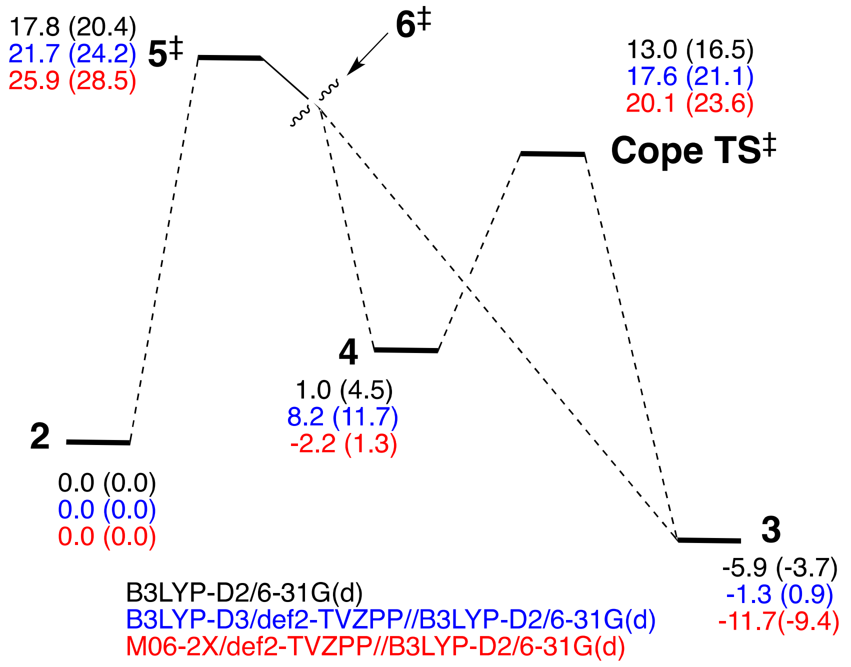
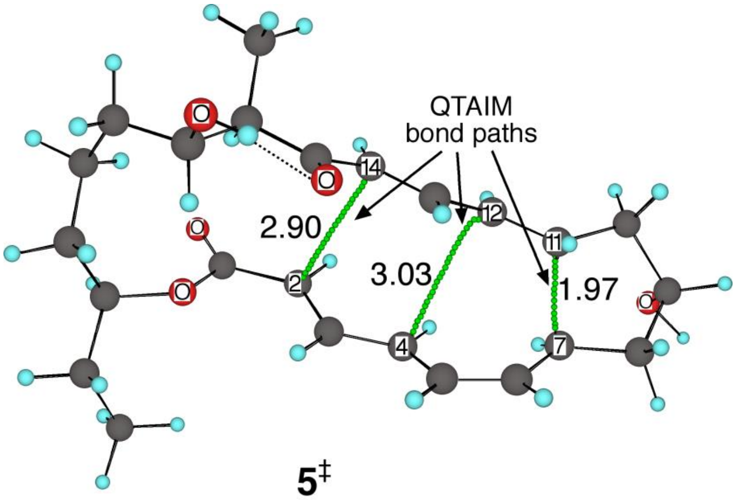


Figure 5.2. Potential energy and free energy (in parentheses, kcal/mol) diagram for the cycloaddition of **2.** Standard optimization and frequency calculations were performed on all stationary points using B3LYP-D2/6-31G(d). Single point energy calculations were performed using B3LYP-D3 and M06-2X with def2-TVZPP basis set for corrections.

The frequent involvement of bispericyclic transition states and bifurcating energy surfaces represents a significant complication in the modern understanding of the Diels-Alder reaction because the product ratio cannot be predicted with conventional transition state theory. A new and intriguing characteristic of the bispericyclic transition structures here is that they combine *[6+4] character* with [4+2] character. Like their [4+2] counterparts, [6+4] cycloadditions are formally allowed as concerted reactions by the Woodward-Hoffman rules but their observation has been rare.[144] The combination of [6+4] with [4+2] character in **5**‡ can be recognized from its unusual geometry. In **5**‡, there are *three* partially formed sigma bonds, C^7-C^{11}, C^4-C^{12}, and C^2-C^{14}, instead of the two partially formed bonds present in a typical Diels-Alder transition state. Within the framework of the Quantum Theory of Atoms in Molecules (QTAIM), [145] each pair of carbons is connected by a bond path. The full formation of the C^7-C^{11} and C^4-C^{12} bonds would complete a [4+2] cycloaddition but the alternative formation of the C^7-C^{11} and C^2-C^{14} bonds would complete a [6+4] cycloaddition. The [4+2] cycloadduct derived from **5**‡ is the experimentally observed single product **3**; transition structures that would lead to stereoisomers of **3** were substantially higher in energy. However, the bispericyclic character of **5**‡ suggests that it can also lead to the [6+4] cycloadduct **4**. Conventional computational analyses would in fact only expect the [6+4] cycloaddition since the steepest-descent path in mass-weighted coordinates (the minimum-energy path, or MEP) starting from **5**‡ leads to **4**. Due to the strain inherent in the 10- and 11-membered rings of **4**, it is 8-11 kcal/mol less stable than **3**. Since **4** can undergo a facile Cope rearrangement (via **Cope TS**, not shown) to afford **3**, it is unclear whether **4** should be observable under the reaction conditions.



5‡

Figure 5.3. The bispericyclic transition structure **5**‡**.** The interatomic distances (in Å) and QTAIM bond paths are shown.

Dynamic trajectory calculations were employed to gain insight into the nature of the cycloaddition and the competition between formation of [6+4] and [4+2] products. Quasiclassical direct-dynamics[146] trajectories on a B3LYP-D2/6-31G(d) energy surface were initiated from the area of **5**‡, giving each real normal mode in **5**‡ its zero-point energy (ZPE) plus a Boltzmann sampling of additional energy appropriate for 25 °C, with a random phase. The transition vector was given a Boltzmann sampling of energy, and the trajectories were integrated both forward and backward in time until either **3** or **4** were formed or **2** was reformed.

Discussion

The trajectories provided a series of striking observations. The first is that there are *three* outcomes of trajectories passing through **5**‡. Out of 353 trajectories, 223 (63%) afforded the [6+4] product **4**, 88 (25%) afforded the Diels-Alder adduct **3** and 42 (12%) *recrossed*, fully forming the C^7-C^{11} bond before passing back through the transition state to reform the starting material. A second observation is that the time required for formation of either **3** or **4** is unusually long. The median times for formation of **3** and **4** starting from the initialization at **5**, defined by the time required for both new sigma bonds to reach carbon-carbon distances of less than 1.7 Å, was 197 and 171 fs, respectively. Over 20% of the trajectories require greater than 300 fs to afford **3**. Simple Diels-Alder reactions typically require only about 50 fs to form product from the transition state.[147] Another way to examine this time is to define a "transition region" from geometries accessible at the transition state within the harmonic approximation, then assess the time required by trajectories to traverse the transition region. When this is done, the median times in the transition region for trajectories leading to **3** and **4** are 130 and 127 fs, respectively, compared to 50-95 fs in other Diels-Alder reactions. A third observation is that the time gap between formation of the first new sigma bond in the cycloadduct (the C^7-C^{11} bond) and formation of the second new sigma bond (either C^4-C^{12} for **3** or C^2-C^{14} for **4**, defined by interatomic distances <1.7 Å) is exceptionally long, with median times of 173 and 139 fs for **3** and **4**, respectively. For comparison, simple symmetrical Diels-Alder reactions exhibit median time gaps of less than 5 fs while unsymmetrical cycloadditions exhibit median time gaps of 10-25 fs.

The paths taken by the trajectories illustrate the dynamical nature of the cycloaddition process in this reaction. Figure 5.4(a) shows a plot of selected trajectories in three dimensions, defined by the C^7-C^{11}, C^4-C^{12}, and C^2-C^{14} internuclear distances, while figure 5.4(b) shows a plot of 30 randomly chosen trajectories. Starting in the area of **2**, the trajectories proceed by the approach of C^7 and C^{11}, passing through the cycloaddition transition state when the C^7-C^{11} distance is about 1.97 Å, then fully forming the C^7-C^{11} bond. The structure that results is geometrically delineated, albeit loosely so, by C^4-C^{12} and C^2-C^{14} distances between 2.8 and 3.2 Å. This structure tends to persist for a few bond vibrations, and it may undergo three distinguishable reactions, i. e., formation of **3**, formation of **4**, and transition state recrossing to the starting **2**. From these properties, the structure is best understood as an intermediate. However, there is no potential-energy barrier for the formation of either of the C^4-C^{12} and C^2-C^{14} bonds from this intermediate. Trajectories persist in this area, briefly, because the route to the two products must pass through a dynamical bottleneck. In qualitative terms, the C^4-C^{12} and C^2-C^{14} atom pairs are energetically attracted but the consummation of their bond formation requires the chance event that one or both of the pairs of atoms specifically approach each other while the C^7-C^{11} distance is in a limited range.

A more quantitative, statistical approach to understanding the nature of the mechanism was pursued by applying canonical variational transition state theory (VTST). [148-150] In transition state theory, the "transition state" is a multidimensional hypersurface dividing the starting material from the product and the properties of the hypersurface are used to calculate the rate constant. In canonical VTST, the position of the transition state hypersurface is varied so as to minimize the rate constant at the reaction temperature. The resulting variational transition states are dynamical bottlenecks and correspond to maxima in the free energy along an MEP connecting the starting material to the product. The critical observation in the cycloaddition of **2** is that there are two variational transition states / dynamical bottlenecks along the MEP. The first corresponds closely to the potential-energy saddle point **5**‡ but the second, structure **6**‡ (Figure 5.5), occurs after the C^7-C^{11} bond is fully formed. The structural area "between" **5**‡ and **6**‡ is not well-defined, but the MEP passing through this area exhibits a shallow minimum in the generalized free energy. This minimum can formally be considered as an intermediate. From this statistical perspective, the intermediate arises because the formation of either the C^4-C^{12} or C^2-C^{14} bonds restricts motions in a way that loses entropy, and the intermediate is delimited at **6**‡ by this entropic barrier. The return to **2** requires traversal of a potential-energy barrier, but this process gains entropy and so is competitive with the downhill paths to **3** and **4**.

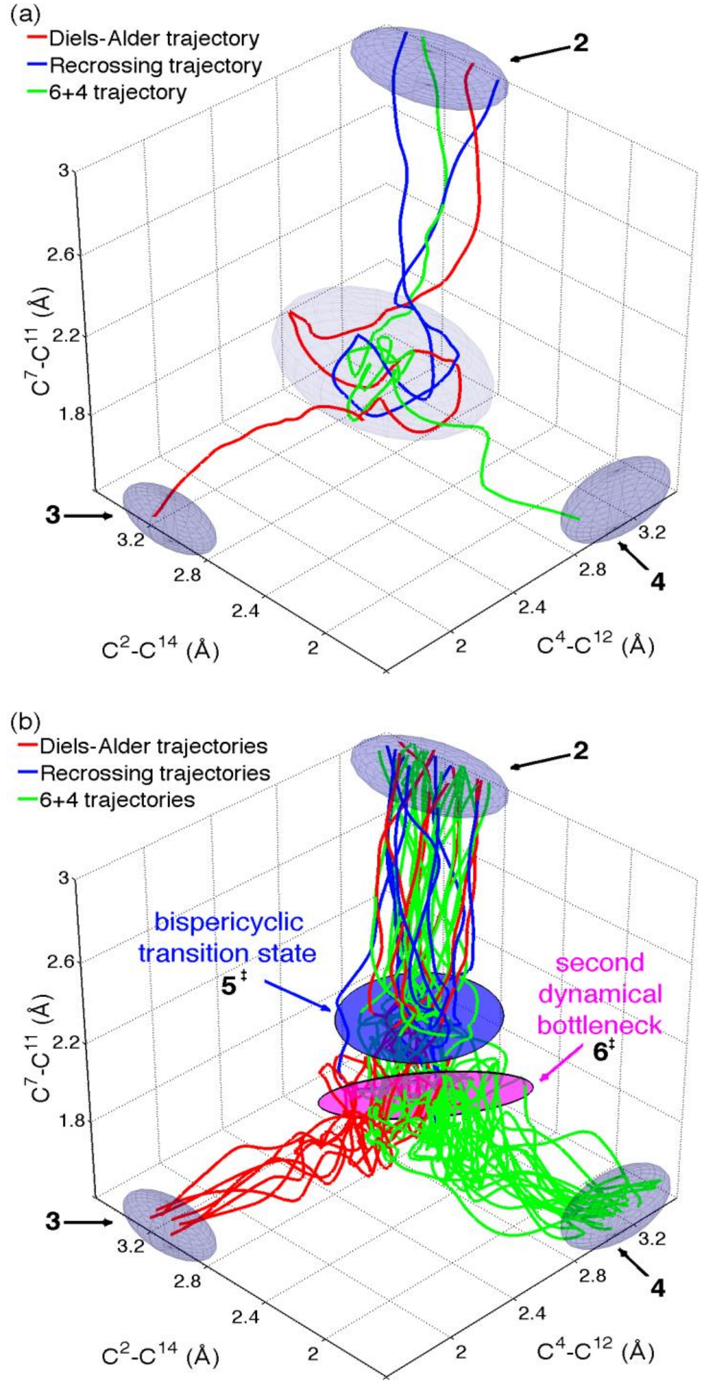
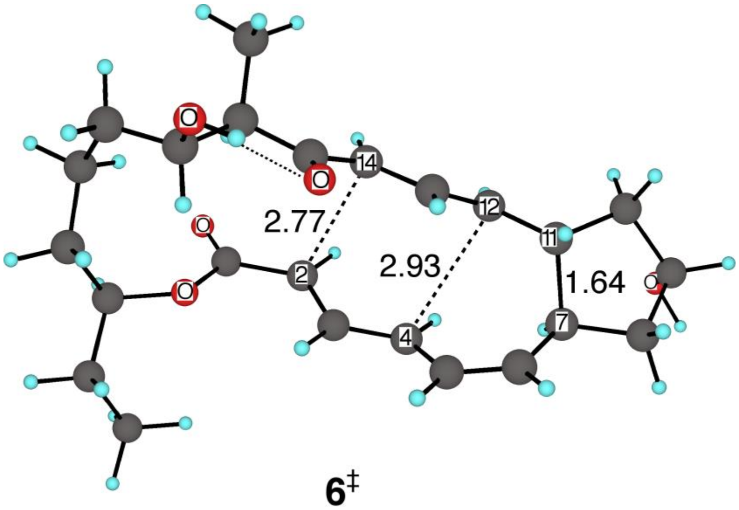


Figure 5.4. Trajectory plots following the C-C interatomic distances. (a). Three selected trajectories. Trajectories pass into an area with a fully-formed C^7-C^{11} bond, then may form **3** or **4** or recross to **2**. (b). Thirty randomly chosen trajectories.

The statistical picture agrees well with the qualitative picture derived from the trajectories. The observation that trajectories tend to persist in an area after fully forming the C^7-C^{11} bond may be viewed as the simple consequence of statistical free-energy barriers for their further conversion or return to reactants. The statistical picture automatically anticipates that an intermediate could proceed either forward to products or backward to starting materials, and that is seen in the trajectories. Quantitatively, there is some difference in the statistical and dynamical predictions. In the harmonic and canonical approximations, the second bottleneck **6**‡ is 2.4 kcal/mol below **5**, so only about 2% recrossing would be expected instead of the 12% observed in the trajectory study. We cannot distinguish whether this difference in the statistical versus the dynamical predictions is due to non-statistical dynamics versus simply being a result of the approximations inherent in the harmonic statistical calculation.



6‡

Figure 5.5. Variational transition state / dynamical bottleneck **6**‡**.** Trajectories passing through **6**‡ may still form either **3** or **4**, but after **6**‡ they do not return to **2**.

A final surprising mechanistic complexity can be discerned from the combination of statistical and trajectory analyses, and that is that the partitioning between **3** and **4** is unrelated to any statistical bottleneck. A plot of sample trajectories on a potential energy surface, as in Figure 5.6, illustrates this idea. Some product-forming trajectories pass quickly through the areas of **5**‡ and **6**‡, but many meander in the area between these two bottlenecks. Structure **6**‡ then represents the furthest reach of those trajectories that ultimately recross **5**‡. The trajectories leading to the Diels-Alder product **3** versus the [6+4] product **4** remain intertwined until *after* **6**‡. In the area after **6**‡, some trajectories proceed directly to **4** while others approach the saddle point for the Cope interconversion of **3** and **4**, **Cope TS**, from above. The **Cope TS** then serves as the dividing knife that separates trajectories that afford **3** from those that afford **4**. VTST could in principle allow a prediction of the ratio of products **3** and **4** if there were separate bottlenecks for the formation of each.[151] However, all attempts to locate a bottleneck specific to the formation of **3** were unsuccessful; steepest-descent paths initiated from the transition state "ridge" associated with **5**‡, as illustrated in Figure 5.6, do encounter bottlenecks in VTST calculations but the bottlenecks are continuous with **6**‡. Thus, while statistical theory can account for some of the recrossing to reform **2** it provides no guidance on the ratio of products **3** and **4**.

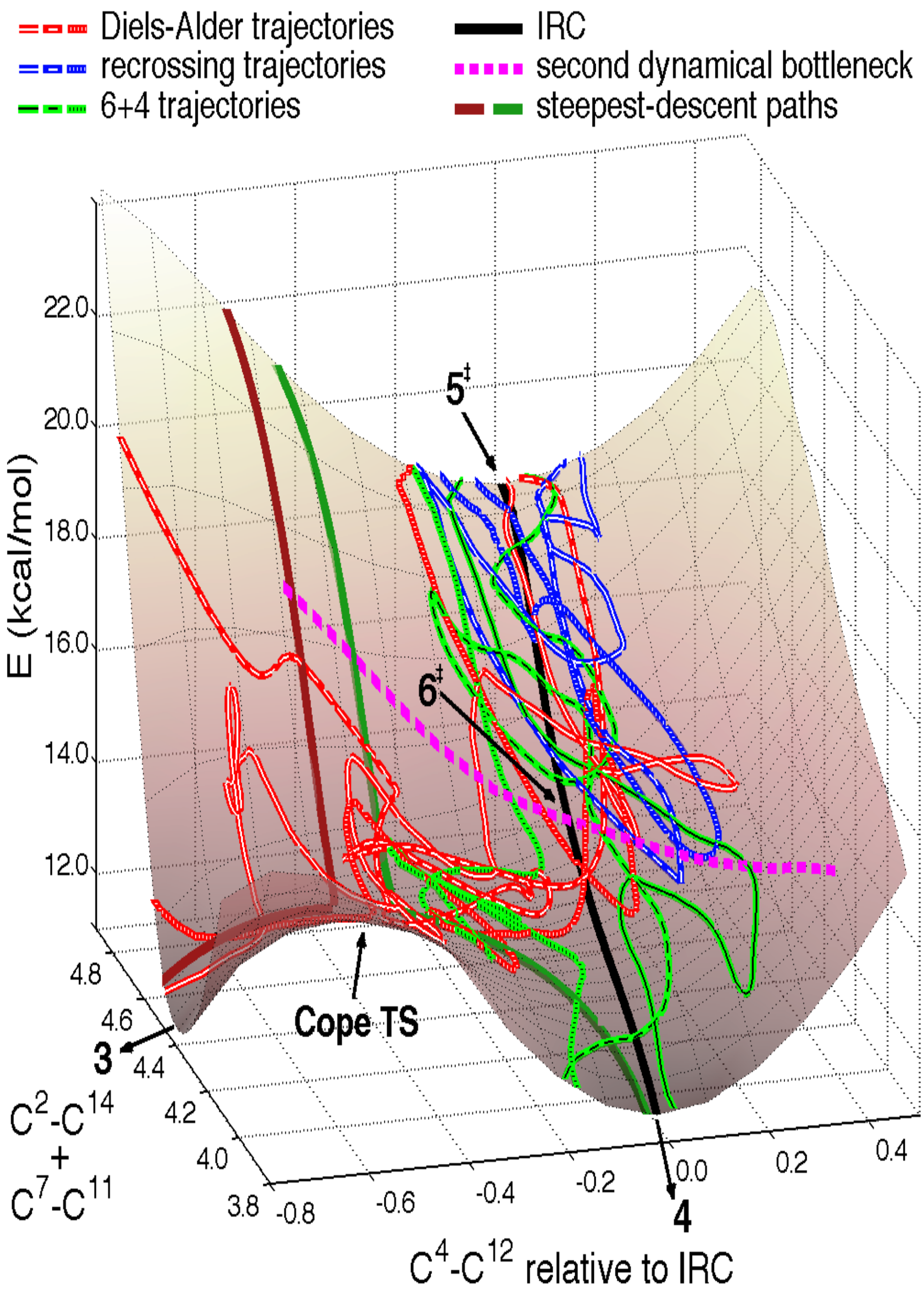


Figure 5.6. Trajectories on a potential energy surface. The 183 coordinate dimensions of the molecule have been reduced to two by fixing the C^2-C^{14} and C^7-C^{11} distances at values in the IRC then scanning the C^4-C^{12} distance relative to the IRC, with all other coordinates minimized. Trajectories meander in the area between **5**‡ and **6**‡, then either revert to **2** or pass through **6**‡ then diverge to **3** or **4**.

Conclusion

Mechanistic chemistry frames the division of reactions into concerted versus two-step processes at a paradigm level. As a result, the assignment of the correct category has been one of the central endeavors of mechanistic research. This context underlies the historical restriction of Diels-Alder reactions to concerted mechanisms. That is, the questions of whether a reaction is a Diels-Alder reaction and whether an enzyme is a "Diels-Alderase" have been assumed to be well-defined and fully resolvable, at least in principle. This is not to imply any simplism; it has been well understood that unambiguous mechanistic knowledge is limited and that reactions may at times proceed by a mixture of mechanisms or by a mechanism that is arbitrarily close to the concerted/two-step borderline. However, the conventional concerted / two-step platonic ideals are simply inadequate to describe the defiantly complex cycloaddition of **2**. In contrast to the stepwise-mechanism ideal, the cycloaddition of **2** involves two cyclic arrays of bonding interactions at its transition state, and one or the other of these arrays is maintained along the paths to the products. There is no opportunity for an "intermediate" to be trapped or lose its stereochemistry; the intermediate itself has no potential-energy minimum and has no parallel in the ions or radicals of ordinary reactive-intermediate chemistry. In contrast to the ideal of a concerted Diels-Alder mechanism, the cycloaddition of **2** involves a free-energy minimum along the reaction pathway. The structure associated with this minimum has a significant lifetime and can ultimately evolve along multiple pathways, a venerable indicator of an intermediate. The reaction also involves two cyclic arrays of bonding interactions at its transition state, as opposed to one in the concerted ideal. As a result, even the seemingly ordinary stepwise mechanism forming **3** via long-lived **4** occurs through the same initial transition state and same second bottleneck as trajectories that reach **3** over a range of 80 to 480 fs.

The mechanism of the SpnF-catalyzed cycloaddition of 2 is unknown, and it need not of course closely resemble the uncatalyzed gas-phase mechanism calculated here. However, if one is to understand exactly what enzymes do, it seems incumbent to recognize the full mechanistic complexity that is possible in uncatalyzed reactions. For example, when a reaction involves a dynamic selection among products on the downhill slope of an energy surface, as seen here and in a growing number of reactions, an enzyme's purpose might go beyond the acceleration of reactions to the control of the "slalom" course choosing among products. Such possibilities are entirely distinct from the lowering of reaction barriers that is assumed to completely define catalysis, but they are recognizable when the dynamic complexity of real reactions is considered.

SUMMARY AND CONCLUSION

Experimental observations and theoretical calculations have always been the two keys to open the treasure chests of reaction mechanisms. Thus the reaction mechanism is established based on correct interpretation of experimental observations and rational thinking of chemical reactions. The mechanisms of various [2+2] cycloaddition and enzymatic reaction were explored in depth using a combination of experimental kinetic isotope effects (KIEs) and trajectory simulations.

Experimental KIEs in thermal [2+2] cycloaddition between allenic compounds showed that these reactions proceeded through a stepwise mechanism via a diradical intermediate. Although some reactions exhibited high stereo specificity, this observation is not conclusive for a concerted mechanism. A more direct evidence for the stepwise mechanism is the isolation of an intermediate derivative in the reaction. Theoretical calculations also supported the stepwise mechanism. This result suggests a careful interpretation of contradictory experimental observations when developing a reaction mechanism. In this case, the stereospecificity may come from a short lived intermediate, not necessarily from a concerted process. In order to clearly understand a reaction, the proposed mechanism should explain all experimental observations, not most of them.

In lewis acid catalyzed [2+2] cycloaddition between allene and alkenes, we observed inversed intramolecular KIEs. Conventional transition state theory was not able to explain this observation, and we proposed a refined model which considered dynamic effects-non statistical recrossing. This improvement successfully explained the experimental observation and gave close predictions to the KIEs. We also proposed a bifurcating energy surface model to understand the regioselectivity in the reaction between allene and pseudo-symmetrical alkenes. This work showed that our current theory is not perfect to explain and understand all experimental observations. Dynamic effects have to be considered for a better description of reaction mechanisms.

Wittig olefination also possesses intrinsic complexity in the mechanism. Early studies proposed the formation of oxaphosphetane undergo a stepwise process via the betaine intermediate, but this proposal was questioned based on a series of experimental observations after 1980s. Currently, literature favors a concerted pathway for the formation of oxaphosphetane over a stepwise one. But again, the experimental observations turned out to be non-conclusive for this mechanism. Based on our experimental KIEs and theoretical calculations, the results are consistent with a stepwise process and the intermediacy of the betaine. The combination of experimental observations and theoretical calculations successfully delineated the mechanism in stabilized Wittig olefinations.

The biosynthesis of spinosyn A has provoked a lot of important discoveries, for example, the standing alone Diels-Alderase SpnF was found to catalyze the cycloaddition step in this process. This discovery led us to a detailed study of the mechanism of the cycloaddition step. The mechanism involves complicated dynamic features and can not be simply understood by conventional transition state theory. In order to fully understand the reaction mechanism, we have not only to consider the stationary points along the reaction coordinate, but also the detailed motion of molecules passing through the transition state and the shape of the energy surface. By understanding of the complexity in the mechanism, this work should be able to aid in probing the function of the enzyme and further manipulations of the process.

Overall, mechanistic studies of organic reactions are very important and useful to improve our abilities of designing and processing chemical reactions. Experimental probes and theoretical predictions are well combined to explore the reaction and provide detailed information of the mechanism. We have utilized experimental KIEs and trajectory simulations to successfully illustrate the mechanisms of various [2+2] cycloadditions.

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APPENDIX

General Computing Procedure

Calculations of structures, energies, and frequencies employed standard procedures in Gaussian09 (S1) unless otherwise noted. Complete structures and energetics are provided in a section below. The program suite PROGDYN used for dynamics is listed at the end of the Supporting Information as a series of component programs as either Unix shell scripts or awk programs. Gaussian09 was used to calculate the forces at each point in trajectories. The latest version of this program can be obtained by emailing Daniel Singleton at singleton@mail.chem.tamu.edu. The original version of this program is published in this section.

The trajectories simulations used in this dissertation are quasi-classical, i. e. including zero-point energy. For trajectories starting at the transition state, the desired energy in each of the normal modes was mapped from a random number generator to a Boltzmann distribution. The phase of each of the normal modes was mapped from Gaussian distribution of random numbers. This distribution is not correct for a classical oscillator but would be approximately correct for a quantum oscillator in its ground state (only ignoring mode displacements outside of the classical limit), and has the advantage that a larger portion of the trajectories start with an energy approximating the initially desired energy. Because of the anharmonicity of the lowest-energy modes, the choice of a random phase for these modes led to a problem for some trajectories, as the energy of the starting point structure for trajectories would inevitably be far from its desired value. To avoid this problem, the mode displacements were turned off for frequencies less than 100 cm^{-1}. (In other words, the mode phases for the lowest-energy modes were initialized only 0 or 180°. After an energy/force calculation on the initial geometry, the total initial energy was calculated and the trajectory was thrown out if the energy did not agree satisfactorily (within 1 kcal/mol) with the desired energy.

A number of the calculations in the dissertation made use of the POLYRATE. These programs were modified in minor ways. In particular, the subroutine mepout was modified to output frequencies with higher precision, and the utility program shuttle was modified to save copies of all frequency calculations so that data could be extracted from them later. To show the complete set of options selected for these calculations, a sample set of input files for POLYRATE are given in a later section. For the sake of simplicity, the starting material in these calculations was generally taken to be a minimized loose complex of reactants. Such complexes are not kinetically significant but this does not matter for the purpose at hand.

Part I

allene sm
CASSCF(4,4)/6-31G*

```
Zero-point correction= 0.056811 (Hartree/Particle)
Thermal correction to Energy= 0.060825
Thermal correction to Enthalpy= 0.061769
Thermal correction to Gibbs Free Energy= 0.032462
Sum of electronic and ZPE= -115.857212
Sum of electronic and thermal Energies= -115.853198
Sum of electronic and thermal Enthalpies= -115.852254
Sum of electronic and thermal Free Energies= -115.881561

     E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 38.168 12.234 61.682
 6    0      -0.000022   -0.000330   -0.000807
 6    0       1.333176    0.000045    0.000262
 6    0      -1.333151    0.000079    0.000196
 1    0       1.887584   -0.458348   -0.798393
 1    0       1.885932    0.459291    0.799619
 1    0      -1.886899    0.799186   -0.458364
 1    0      -1.886635   -0.798899    0.459237
Zero-point correction= 0.056503 (Hartree/Particle)
Thermal correction to Energy= 0.060548
Thermal correction to Enthalpy= 0.061492
Thermal correction to Gibbs Free Energy= 0.032113
Sum of electronic and ZPE= -115.869327
Sum of electronic and thermal Energies= -115.865282
Sum of electronic and thermal Enthalpies= -115.864338
Sum of electronic and thermal Free Energies= -115.893717

     E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 37.995 12.270 61.833

6 -0.000022 -0.000330 -0.000807
6 1.333176 0.000045 0.000262
6 -1.333151 0.000079 0.000196
1 1.887584 -0.458348 -0.798393
1 1.885932 0.459291 0.799619
1 -1.886899 0.799186 -0.458364
1 -1.886635 -0.798899 0.459237
```

```
6 -0.000022 -0.000330 -0.000807
6 1.333176 0.000045 0.000262
6 -1.333151 0.000079 0.000196
1 1.887584 -0.458348 -0.798393
1 1.885932 0.459291 0.799619
1 -1.886899 0.799186 -0.458364
1 -1.886635 -0.798899 0.459237
```

allene int1

CASSCF(8,8)/6-31G*

```
Zero-point correction= 0.119042 (Hartree/Particle)
Thermal correction to Energy= 0.125735
Thermal correction to Enthalpy= 0.126680
Thermal correction to Gibbs Free Energy= 0.089101
Sum of electronic and ZPE= -231.715995
Sum of electronic and thermal Energies= -231.709302
Sum of electronic and thermal Enthalpies= -231.708358
Sum of electronic and thermal Free Energies= -231.745936

     E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 78.900 26.151 79.091
Zero-point correction= 0.118563 (Hartree/Particle)
Thermal correction to Energy= 0.125270
Thermal correction to Enthalpy= 0.126214
Thermal correction to Gibbs Free Energy= 0.088405
Sum of electronic and ZPE= -231.737815
Sum of electronic and thermal Energies= -231.731109
Sum of electronic and thermal Enthalpies= -231.730164
Sum of electronic and thermal Free Energies= -231.767974

     E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 78.608 26.108 79.576
```

allene dimer ts2

CASSCF(8,8)/6-31G*

```
Zero-point correction= 0.119616 (Hartree/Particle)
Thermal correction to Energy= 0.125858
Thermal correction to Enthalpy= 0.126802
Thermal correction to Gibbs Free Energy= 0.090313
Sum of electronic and ZPE= -231.694260
Sum of electronic and thermal Energies= -231.688018
Sum of electronic and thermal Enthalpies= -231.687073
Sum of electronic and thermal Free Energies= -231.723562
```

```
     E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 78.977 23.914 76.797
Zero-point correction= 0.119232 (Hartree/Particle)
Thermal correction to Energy= 0.125425
Thermal correction to Enthalpy= 0.126369
Thermal correction to Gibbs Free Energy= 0.089983
Sum of electronic and ZPE= -231.720981
Sum of electronic and thermal Energies= -231.714787
Sum of electronic and thermal Enthalpies= -231.713843
Sum of electronic and thermal Free Energies= -231.750229

     E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 78.706 23.756 76.581
```

allene dimer tsr
CASSCF(8,8)/6-31G*

```
Zero-point correction= 0.118533 (Hartree/Particle)
Thermal correction to Energy= 0.124597
Thermal correction to Enthalpy= 0.125541
Thermal correction to Gibbs Free Energy= 0.089623
Sum of electronic and ZPE= -231.714746
Sum of electronic and thermal Energies= -231.708682
Sum of electronic and thermal Enthalpies= -231.707738
Sum of electronic and thermal Free Energies= -231.743656

     E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 78.186 24.279 75.596
Zero-point correction= 0.118132 (Hartree/Particle)
Thermal correction to Energy= 0.124176
Thermal correction to Enthalpy= 0.125120
Thermal correction to Gibbs Free Energy= 0.089223
Sum of electronic and ZPE= -231.737281
Sum of electronic and thermal Energies= -231.731237
Sum of electronic and thermal Enthalpies= -231.730293
Sum of electronic and thermal Free Energies= -231.766190

     E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 77.921 24.177 75.552
```

dimethylallene+dmfumarate_product2_trans opt
ub3lyp/6-31G*
E(UB3LYP) = -729.682516214

Zero-point correction= 0.258323 (Hartree/Particle)
Thermal correction to Energy= 0.275469
Thermal correction to Enthalpy= 0.276413
Thermal correction to Gibbs Free Energy= 0.210982
Sum of electronic and ZPE= -729.424193
Sum of electronic and thermal Energies= -729.407047
Sum of electronic and thermal Enthalpies= -729.406103
Sum of electronic and thermal Free Energies= -729.471534

```
     E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 172.860 59.484 137.713
```

```
C,0,-1.6162713271,3.2564049375,-1.36044323
C,0,-1.0106749869,2.2022689395,-0.8060764623
C,0,0.246337773,2.0524149042,0.0376478523
H,0,1.1829393796,2.4171482288,-0.397529077
C,0,0.0545125832,0.498142107,-0.0359093448
C,0,-1.305613743,0.6908827986,-0.7570724443
C,0,-1.4099870093,-0.0325872683,-2.0845886313
O,0,-0.47152723,-0.3597382873,-2.7798350234
C,0,0.000043503,-0.2195725706,1.2894413759
O,0,-1.006801948,-0.5720792057,1.8675363023
O,0,1.2450898334,-0.396911338,1.7862107891
C,0,1.3106814919,-1.0331225792,3.0730958399
O,0,-2.69901763,-0.2707442229,-2.4207812937
C,0,-2.8947144854,-0.9261680579,-3.6856548433
H,0,0.1583977811,2.4614875156,1.0519260804
H,0,0.7980425232,0.0326480172,-0.6864032187
H,0,-2.1595365094,0.4333475491,-0.1229895749
C,0,-2.8937511491,3.1521117879,-2.1547752454
C,0,-1.0489836246,4.646731758,-1.2088881326
H,0,-3.9734952472,-1.0463852833,-3.7884582531
H,0,-2.495143538,-0.3166466383,-4.5005853492
H,0,-2.3963210186,-1.8988989023,-3.6926053034
H,0,2.3717312745,-1.0886415964,3.3182904585
H,0,0.7729997354,-0.444848004,3.8216770704
H,0,0.873641907,-2.0343075304,3.0292704255
H,0,-3.6742300846,3.7865593952,-1.7118417321
H,0,-2.7461155191,3.5142264877,-3.182169833
```

H,0,-3.273535667,2.1294760623,-2.2050388522
H,0,-0.8441118639,5.0952871469,-2.1909675078
H,0,-1.7672148412,5.3097067593,-0.7065194474
H,0,-0.1194623627,4.6575590899,-0.6322873945

dmallene+dmmaleate_2+2_pdt_1.log
dimethylallene+fumarate_product2_cis opt
ub3lyp/6-31g*
E(UB3LYP) = -729.680227118

Zero-point correction= 0.258407 (Hartree/Particle)
Thermal correction to Energy= 0.275404
Thermal correction to Enthalpy= 0.276348
Thermal correction to Gibbs Free Energy= 0.212583
Sum of electronic and ZPE= -729.421820
Sum of electronic and thermal Energies= -729.404823
Sum of electronic and thermal Enthalpies= -729.403879
Sum of electronic and thermal Free Energies= -729.467644

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	172.819	59.490	134.206

C,0,1.7952873832,-0.5976150678,3.3311206297
O,0,1.4218209229,0.257567297,2.2382649837
C,0,0.9191955998,-0.377604616,1.1609747883
O,0,0.8254016599,-1.5829249097,1.0668258804
C,0,0.5462666606,0.5826183299,0.0534439288
C,0,-0.848362408,0.3890569389,-0.627437618
H,0,-0.8514004261,-0.1095444361,-1.5992366005
C,0,0.204909415,2.0719459401,0.3379067518
C,0,-0.9604689477,1.9240921482,-0.6281736273
C,0,-1.7286417377,2.7721897461,-1.3170811475
C,0,-1.5688185897,4.266442235,-1.1855922336
C,0,-2.7985405618,2.2994004012,-2.2699527011
H,0,0.9790788633,2.8084168298,0.0982058873
H,0,-0.114307578,2.2202935133,1.3749259317
H,0,1.3228003852,0.4990925795,-0.7152807309
C,0,-1.8863667482,-0.2391530464,0.2815585481
H,0,2.1777250523,0.0676263437,4.1059316405
H,0,0.9244620705,-1.1503258276,3.6925701812
H,0,2.5648783482,-1.3085429652,3.0185043702
H,0,-2.5922749044,2.6400705055,-3.2945378398
H,0,-2.8947595733,1.2104770542,-2.2811330891

H,0,-3.7760386701,2.7189245989,-1.9942641957
H,0,-1.3561251194,4.7265597089,-2.1607874112
H,0,-2.4956462676,4.7282079539,-0.8178729754
H,0,-0.7626463795,4.5378866069,-0.4980328866
O,0,-1.9149645793,-0.127535641,1.489426488
O,0,-2.8233298266,-0.9015615842,-0.4304617423
C,0,-3.8837504173,-1.4868099226,0.3453278824
H,0,-4.5367741621,-1.9779218762,-0.3766020025
H,0,-3.479012116,-2.212097768,1.0555648682
H,0,-4.427874348,-0.7143240705,0.8951870413

dimethylallene+fumarate_product_trans opt freq
m062x/6-31+G**
E(RM062X) = -729.408876752

Zero-point correction= 0.259415 (Hartree/Particle)
Thermal correction to Energy= 0.276079
Thermal correction to Enthalpy= 0.277024
Thermal correction to Gibbs Free Energy= 0.214589
Sum of electronic and ZPE= -729.149462
Sum of electronic and thermal Energies= -729.132797
Sum of electronic and thermal Enthalpies= -729.131853
Sum of electronic and thermal Free Energies= -729.194287

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 173.242 59.516 131.404

C,0,0.1269943245,0.4558196638,-0.1361927948
C,0,0.1156192695,-0.2048539648,1.2110592028
H,0,0.8174494064,-0.0658043416,-0.8050699053
O,0,1.3650711024,-0.3808385253,1.6729399177
O,0,-0.8722901512,-0.5025602119,1.8412515562
C,0,-1.2348420777,0.6936249538,-0.8029278305
C,0,-1.5635785464,-0.1638022582,-1.9945460294
H,0,-2.0610029979,0.6628951518,-0.0830973156
O,0,-2.7325742003,0.2044909059,-2.5426143126
O,0,-0.8704742246,-1.0496122539,-2.4343130484
C,0,0.3937806527,2.0084347751,-0.1432330556
C,0,-0.7759293422,2.1133333348,-1.1128203289
C,0,-1.1540160917,3.0233069157,-2.000746773
H,0,-2.0106259806,2.8550511371,-2.646580478
H,0,-0.6127011199,3.9601271167,-2.1032134611
C,0,0.0729590539,2.6693235923,1.1999385653

```
C,0,1.7561112188,2.4397156712,-0.664268488
H,0,1.7955970088,3.5283481757,-0.7806322313
H,0,2.5409840493,2.1425644766,0.0396304322
H,0,1.9661158339,1.9833188457,-1.6357783184
H,0,0.0670918537,3.757404241,1.0845209339
H,0,-0.9068867441,2.361414819,1.5780818323
H,0,0.8305337387,2.4033400862,1.9461778224
C,0,-3.1160633128,-0.5278432232,-3.7102646423
H,0,-4.0828577401,-0.1251478671,-4.0065779318
H,0,-2.3769937513,-0.3873335098,-4.5021117962
H,0,-3.193928495,-1.5919799676,-3.4786726911
C,0,1.4589283174,-0.9476429751,2.9823460161
H,0,2.5237027971,-1.038374157,3.1885675405
H,0,0.9775995357,-0.2933804482,3.71297249
H,0,0.974946613,-1.9260991589,3.0058751227
```

dimethylallene+fumarate_product_cis opt freq
m062x/6-31+G**
E(RM062X) = -729.408172862

```
Zero-point correction= 0.259909 (Hartree/Particle)
Thermal correction to Energy= 0.276687
Thermal correction to Enthalpy= 0.277631
Thermal correction to Gibbs Free Energy= 0.214792
Sum of electronic and ZPE= -729.148264
Sum of electronic and thermal Energies= -729.131486
Sum of electronic and thermal Enthalpies= -729.130542
Sum of electronic and thermal Free Energies= -729.193381
```

```
      E       CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 173.623 59.090 132.256
```

```
C,0,1.6775690446,-0.6375251309,3.3079601045
O,0,1.3674986123,0.2455011321,2.2274794474
C,0,0.9780150365,-0.3592173118,1.0997206475
O,0,0.965480011,-1.5586867052,0.9487629118
C,0,0.5936370053,0.6153749972,0.0162615239
C,0,-0.785396452,0.3801603515,-0.6572055073
H,0,-0.8002193395,-0.1211127007,-1.6264497592
C,0,0.1900736045,2.0712020377,0.3503988397
C,0,-0.9497266602,1.9032065943,-0.6367982138
C,0,-1.7346205439,2.7281691462,-1.3281213298
C,0,-1.6409638454,4.2210873092,-1.1668466403
```

C,0,-2.7614300123,2.2235181549,-2.3055281653
H,0,0.9311018438,2.848140947,0.146990883
H,0,-0.1566039325,2.1556013422,1.3853406605
H,0,1.3750991402,0.5815069847,-0.7488127205
C,0,-1.7903222929,-0.2451599363,0.2799349273
H,0,1.975146546,0.0027336495,4.1364659409
H,0,0.7932357262,-1.2235359067,3.5677170953
H,0,2.488298637,-1.313091059,3.0271795775
H,0,-2.5774990069,2.6340802359,-3.3055060204
H,0,-2.7683308307,1.1329776654,-2.3679436147
H,0,-3.7645622708,2.5502940008,-2.0065062035
H,0,-1.408173698,4.6998318523,-2.1254242273
H,0,-2.6001545555,4.6310073556,-0.8294961795
H,0,-0.8751334912,4.5067488493,-0.4422387537
O,0,-1.7153941256,-0.2206690857,1.4869841821
O,0,-2.8239586134,-0.7773743091,-0.3868073824
C,0,-3.8576400421,-1.3315840012,0.4321017089
H,0,-4.6067991434,-1.7132891269,-0.2590046584
H,0,-3.4547014539,-2.1354464134,1.0512551002
H,0,-4.2818018974,-0.5595439186,1.0774288258

dimethylallene+fumarate_product2_cis opt freq
m062x/6-31+G**
E(RM062X) = -729.404018391

Zero-point correction= 0.259286 (Hartree/Particle)
Thermal correction to Energy= 0.275824
Thermal correction to Enthalpy= 0.276768
Thermal correction to Gibbs Free Energy= 0.215166
Sum of electronic and ZPE= -729.144732
Sum of electronic and thermal Energies= -729.128195
Sum of electronic and thermal Enthalpies= -729.127251
Sum of electronic and thermal Free Energies= -729.188852

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 173.082 59.541 129.651

C,0,1.8703959004,-0.690479812,3.1056741242
O,0,1.6919639086,-0.199399477,1.7740781482
C,0,0.4483751162,-0.3238908387,1.2778711018
C,0,0.3676308842,0.3055103987,-0.0839829667
C,0,0.3378746673,1.8799830661,-0.1083773215
C,0,-0.788024957,1.7552789213,-1.1245545187

```
 C,0,-1.3224479526,2.6047458678,-1.9914230282
 H,0,-2.1125995455,2.2993403361,-2.6710983439
 O,0,-0.4585476994,-0.8364532903,1.8898792835
 C,0,-0.9743008695,0.2693810602,-0.880052399
 C,0,-2.1933898323,-0.1091194931,-0.0600520369
 O,0,-2.4441274018,-1.420503032,-0.1736282546
 C,0,-3.4358142671,-1.9215505483,0.7249457078
 H,0,-0.9908110022,3.6386306173,-2.0391631531
 O,0,-2.860136086,0.6484491462,0.6011645457
 H,0,-0.9432558904,-0.3715438377,-1.7644733464
 C,0,1.6198718251,2.5430264312,-0.590489535
 C,0,-0.1436463928,2.4916252744,1.210802996
 H,0,1.1958524665,-0.0675404515,-0.6928333828
 H,0,2.9175548108,-0.5161414517,3.346046915
 H,0,1.2185119237,-0.1506351297,3.796268364
 H,0,1.634708641,-1.7557227939,3.1507769903
 H,0,-3.5116816506,-2.9873067423,0.5160147012
 H,0,-3.1103006486,-1.748645178,1.7534745261
 H,0,-4.3922672937,-1.4233040673,0.554191934
 H,0,-0.3330274207,3.5596581083,1.0649981599
 H,0,-1.0729477534,2.0284401325,1.5531690328
 H,0,0.6260414132,2.3790592587,1.9835405296
 H,0,1.4648694539,3.6191012221,-0.7239245258
 H,0,2.4194487181,2.4022202275,0.1448066521
 H,0,1.9452889345,2.1251290751,-1.5480948995
```

```
dm_fumarate opt+freq
m062x/6-31G*
E(RM062X) = -534.107610631

Zero-point correction= 0.142044 (Hartree/Particle)
Thermal correction to Energy= 0.152740
Thermal correction to Enthalpy= 0.153684
Thermal correction to Gibbs Free Energy= 0.105506
Sum of electronic and ZPE= -533.980749
Sum of electronic and thermal Energies= -533.970053
Sum of electronic and thermal Enthalpies= -533.969109
Sum of electronic and thermal Free Energies= -534.017287

    E     CV       S
  KCal/Mol Cal/Mol-K Cal/Mol-K
Total 95.846 35.981 101.399
Zero-point correction= 0.141024 (Hartree/Particle)
Thermal correction to Energy= 0.150225
```

```
Thermal correction to Enthalpy= 0.151169
Thermal correction to Gibbs Free Energy= 0.106868
Sum of electronic and ZPE= -533.966587
Sum of electronic and thermal Energies= -533.957386
Sum of electronic and thermal Enthalpies= -533.956442
Sum of electronic and thermal Free Energies= -534.000742

      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 94.267 32.235 93.238

 C,0,0.5302786594,0.,-0.0006317942
 C,0,0.5302786594,0.,1.3356317942
 C,0,1.6803600817,0.,-0.9541558594
 C,0,1.6803600817,0.,2.2891558594
 H,0,-0.4346314989,0.,1.8345361079
 O,0,1.1813911071,0.,-2.2103425334
 O,0,2.8569808164,0.,-0.7135338267
 C,0,2.1700940458,0.,-3.236340756
 H,0,1.6222231079,0.,-4.1773661041
 H,0,2.8016808324,0.8879638352,-3.1568497667
 H,0,2.8016808324,-0.8879638352,-3.1568497667
 O,0,1.1813911071,0.,3.5453425334
 O,0,2.8569808164,0.,2.0485338267
 C,0,2.1700940458,0.,4.571340756
 H,0,1.6222231079,0.,5.5123661041
 H,0,2.8016808324,-0.8879638352,4.4918497667
 H,0,2.8016808324,0.8879638352,4.4918497667
 H,0,-0.4346314989,0.,-0.4995361079
```

```
dmallene+fumarate TS1 freq
UB3LYP/6-31G*
E(UB3LYP) = -729.595883425

Zero-point correction= 0.252497 (Hartree/Particle)
Thermal correction to Energy= 0.270399
Thermal correction to Enthalpy= 0.271343
Thermal correction to Gibbs Free Energy= 0.205819
Sum of electronic and ZPE= -729.343386
Sum of electronic and thermal Energies= -729.325484
Sum of electronic and thermal Enthalpies= -729.324540
Sum of electronic and thermal Free Energies= -729.390065

      E      CV        S
```

KCal/Mol Cal/Mol-K Cal/Mol-K
Total 169.678 61.972 137.908

C,0,-0.1887447525,1.1481973908,0.9332231058
C,0,0.2295269855,0.662584668,-0.280198698
C,0,-0.3167744665,0.2789931108,-1.4411306129
H,0,-1.3175996216,0.6007870321,-1.7236465171
H,0,0.2473223426,-0.285313828,-2.1772471458
C,0,2.0934287671,0.2770713752,-0.3179226646
C,0,2.1894596098,-1.124484895,-0.4097683852
C,0,1.9442071737,-1.898265445,0.7865951007
O,0,1.6311023965,-1.4203500894,1.874686495
C,0,2.5953739534,1.0597290433,-1.4956276201
O,0,2.6499146214,0.6581548646,-2.6394289691
O,0,2.9715222161,2.305033558,-1.1229605761
C,0,3.4432689324,3.147144427,-2.1877859414
O,0,2.0718195521,-3.2384335755,0.5796722108
C,0,1.8238491357,-4.0559840643,1.7270796114
C,0,0.5690302522,2.2258216328,1.6532800101
C,0,-1.3056235868,0.4792627587,1.6907233909
H,0,2.3637538166,0.7081235036,0.6401149406
H,0,2.3373238976,-1.6184534534,-1.3620478412
H,0,3.6972143144,4.0977820087,-1.7180917214
H,0,4.3228043813,2.7063287957,-2.6641460026
H,0,2.6630836173,3.2850007911,-2.941227118
H,0,1.9906192327,-5.0830904847,1.3988675797
H,0,2.5058127206,-3.8003732141,2.5436749774
H,0,0.7954640247,-3.9316976633,2.0803587067
H,0,-0.1217330585,2.9091131713,2.1627902538
H,0,1.2052374294,1.7792853196,2.4350365782
H,0,1.2096379294,2.8059571655,0.9843904189
H,0,-2.0524431609,1.2237240185,2.0023227041
H,0,-1.8002801887,-0.2879457811,1.0905009688
H,0,-0.9241414669,0.0052908589,2.6051847604

dmallene+dmmaleate 2+2 intermediate freq
ub3lyp/6-31g*
E(UB3LYP) = -729.609804306

Zero-point correction= 0.253442 (Hartree/Particle)
Thermal correction to Energy= 0.271509
Thermal correction to Enthalpy= 0.272453
Thermal correction to Gibbs Free Energy= 0.204486
Sum of electronic and ZPE= -729.356362

Sum of electronic and thermal Energies= -729.338296
Sum of electronic and thermal Enthalpies= -729.337352
Sum of electronic and thermal Free Energies= -729.405318

```
      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 170.374 62.865 143.048
```

```
C,0,-0.5692032616,2.0552601503,-1.544784515
C,0,0.5989637086,2.0887912982,-0.5901702667
C,0,0.3802749586,1.9824959486,0.7980546191
C,0,-0.8754625303,1.7657010769,1.3420392866
C,0,1.9479087272,2.2672579,-1.2292889833
C,0,1.5449590759,2.0370154891,1.8037390491
C,0,2.4377549321,3.2690258843,1.6241634931
O,0,3.7239645508,2.9998375791,1.9428342987
C,0,4.6192872641,4.1245402528,1.8898067394
C,0,2.2627795689,0.7296650763,1.838837778
C,0,2.1511959089,-0.1299982773,3.0004451116
O,0,1.5282393819,0.1421750114,4.0200984401
O,0,2.0447203749,4.3633763921,1.2917967557
O,0,2.8290868691,-1.2969185167,2.8315556368
C,0,2.769194469,-2.1992586861,3.9432282107
H,0,2.8238299803,0.3725376418,0.9829933288
H,0,-1.0123383159,1.6680445034,2.4135429107
H,0,-1.7627725907,1.6726478905,0.7264930535
H,0,1.1052617036,2.1711533001,2.7999661426
H,0,5.596175005,3.732431732,2.1737411619
H,0,4.6495370837,4.5432466314,0.8805105686
H,0,4.2981133312,4.9018558103,2.587892858
H,0,-0.2493387816,2.286943267,-2.5654979452
H,0,-1.0498098439,1.0661026178,-1.5682651751
H,0,-1.3458728363,2.7792787291,-1.2676360885
H,0,2.0662293505,1.5732114423,-2.0731781881
H,0,2.0510580024,3.2816839976,-1.6440047127
H,0,2.7931089596,2.1075448668,-0.5558141442
H,0,3.3554812478,-3.0698681598,3.6466486919
H,0,3.1940187437,-1.7385317291,4.8398703246
H,0,1.7349259625,-2.4870911203,4.1533115596
```

dmallene+dmmaleate 2+2 opt2 freq
ub3lyp/6-31g*
E(UB3LYP) = -729.532820093

```
Zero-point correction= 0.251217 (Hartree/Particle)
Thermal correction to Energy= 0.268636
Thermal correction to Enthalpy= 0.269580
Thermal correction to Gibbs Free Energy= 0.205501
Sum of electronic and ZPE= -729.281603
Sum of electronic and thermal Energies= -729.264184
Sum of electronic and thermal Enthalpies= -729.263240
Sum of electronic and thermal Free Energies= -729.327319

    E      CV        S
  KCal/Mol Cal/Mol-K Cal/Mol-K
Total 168.572 62.160 134.865

 C,0,-0.3961165348,0.7561255741,-0.8805800282
 C,0,0.6946497987,1.6392819096,-0.312614801
 C,0,1.71518619,2.1400171787,-1.1798280428
 C,0,1.9217429313,1.7136805209,-2.5590125831
 C,0,0.9432880767,1.3868998796,1.1645251714
 C,0,1.9909024459,3.5683949097,-0.7368309996
 C,0,3.1456562619,3.8209595965,0.2318126971
 O,0,3.412183713,5.1409217658,0.2875282828
 C,0,4.3837499123,5.5249179202,1.2735302681
 C,0,0.5687947723,3.7918268015,-0.209358567
 C,0,0.2743509249,4.3300796444,1.1101694763
 O,0,-1.0533130895,4.6254271116,1.2360253293
 C,0,-1.4451335967,5.1146382183,2.5236070081
 O,0,1.0669906597,4.4579961742,2.0352322355
 O,0,3.7754205002,2.9754031468,0.8273817495
 H,0,1.4000736441,2.175984995,-3.3987369873
 H,0,2.684783825,0.9787393031,-2.8104866817
 H,0,-0.1673679323,4.0078689874,-0.9772348272
 H,0,2.1857046939,4.2147918511,-1.6034770647
 H,0,4.494343181,6.6050190345,1.1706337157
 H,0,4.0167392244,5.2686330837,2.2704871041
 H,0,5.3368246308,5.0205594761,1.0946040658
 H,0,-1.319063457,0.8863952888,-0.3040808624
 H,0,-0.6030075409,0.9698607925,-1.9325990102
 H,0,-0.1170900583,-0.3041041661,-0.7975309414
 H,0,0.0171373005,1.4882198523,1.7412823185
 H,0,1.2816571863,0.3451851283,1.2681530929
 H,0,1.7102574254,2.0266389009,1.5953639643
 H,0,-2.5204199376,5.2876707685,2.4575905136
 H,0,-1.2227666206,4.3817981842,3.304858028
 H,0,-0.923477531,6.0466091679,2.7610863757
```

```
dmallene+dmmaleate_2+2_ts2_2.log
 dmallene+dmmaleate 2+2 opt2 freq
ub3lyp/6-31g*
E(UB3LYP) = -729.538062582

Zero-point correction= 0.251456 (Hartree/Particle)
Thermal correction to Energy= 0.268873
Thermal correction to Enthalpy= 0.269817
Thermal correction to Gibbs Free Energy= 0.205250
Sum of electronic and ZPE= -729.286607
Sum of electronic and thermal Energies= -729.269190
Sum of electronic and thermal Enthalpies= -729.268246
Sum of electronic and thermal Free Energies= -729.332812

      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 168.720 61.967 135.892

 C,0,-0.5882478139,1.120591079,-0.67431293
 C,0,0.7108435731,1.7054837528,-0.1658412304
 C,0,1.7376120433,1.92749307,-1.2666239298
 C,0,0.6942667022,2.4731441103,1.0387315419
 C,0,1.9700011485,2.0780953992,1.7982743654
 C,0,2.0960741503,0.7066062458,1.1577529917
 H,0,2.9837791152,0.4613435599,0.5855400614
 C,0,-0.5052462928,2.8895953786,1.7508420857
 C,0,3.1716751841,2.9913963266,1.6347066803
 O,0,4.1306667489,2.7980928256,0.9153635207
 O,0,3.0284449418,4.093176619,2.4004132968
 C,0,4.0871610488,5.0601445521,2.2976612767
 H,0,-0.9619375694,2.2427660174,2.4991324656
 H,0,-0.9097128381,3.8944627138,1.6406000469
 C,0,1.3415550023,-0.380380333,1.7606699796
 H,0,1.7390255246,2.0202293994,2.8683747954
 H,0,3.8071092557,5.8713473906,2.9701611925
 H,0,5.0402622717,4.6197123823,2.6018450868
 H,0,4.1761573133,5.4248597414,1.270781705
 H,0,-0.3887439091,0.2723609752,-1.338595361
 H,0,-1.2301958412,0.7881571383,0.1458724696
 H,0,-1.1441648842,1.8656313567,-1.2617210327
 H,0,1.9309979389,0.9990349873,-1.8145425767
 H,0,1.3151024674,2.647093022,-1.9846601294
 H,0,2.6855644285,2.3265704464,-0.9057872079
```

O,0,1.691928954,-1.5902576695,1.2369269223
O,0,0.4595062077,-0.2533153465,2.6024512408
C,0,0.952637688,-2.7062960518,1.7441077975
H,0,1.3537030748,-3.5821302932,1.2316577268
H,0,1.0856541546,-2.8032496985,2.8256388019
H,0,-0.1154427894,-2.5963300971,1.5330963469

dmallene+dmmaleate 2+2 intermediate freq
ub3lyp/6-31g*
E(UB3LYP) = -729.609804306

Zero-point correction= 0.253442 (Hartree/Particle)
Thermal correction to Energy= 0.271509
Thermal correction to Enthalpy= 0.272453
Thermal correction to Gibbs Free Energy= 0.204486
Sum of electronic and ZPE= -729.356362
Sum of electronic and thermal Energies= -729.338296
Sum of electronic and thermal Enthalpies= -729.337352
Sum of electronic and thermal Free Energies= -729.405318

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	170.374	62.865	143.048

C,0,-0.5692032616,2.0552601503,-1.544784515
C,0,0.5989637086,2.0887912982,-0.5901702667
C,0,0.3802749586,1.9824959486,0.7980546191
C,0,-0.8754625303,1.7657010769,1.3420392866
C,0,1.9479087272,2.2672579,-1.2292889833
C,0,1.5449590759,2.0370154891,1.8037390491
C,0,2.4377549321,3.2690258843,1.6241634931
O,0,3.7239645508,2.9998375791,1.9428342987
C,0,4.6192872641,4.1245402528,1.8898067394
C,0,2.2627795689,0.7296650763,1.838837778
C,0,2.1511959089,-0.1299982773,3.0004451116
O,0,1.5282393819,0.1421750114,4.0200984401
O,0,2.0447203749,4.3633763921,1.2917967557
O,0,2.8290868691,-1.2969185167,2.8315556368
C,0,2.769194469,-2.1992586861,3.9432282107
H,0,2.8238299803,0.3725376418,0.9829933288
H,0,-1.0123383159,1.6680445034,2.4135429107
H,0,-1.7627725907,1.6726478905,0.7264930535
H,0,1.1052617036,2.1711533001,2.7999661426
H,0,5.596175005,3.732431732,2.1737411619

```
 H,0,4.6495370837,4.5432466314,0.8805105686
 H,0,4.2981133312,4.9018558103,2.587892858
 H,0,-0.2493387816,2.286943267,-2.5654979452
 H,0,-1.0498098439,1.0661026178,-1.5682651751
 H,0,-1.3458728363,2.7792787291,-1.2676360885
 H,0,2.0662293505,1.5732114423,-2.0731781881
 H,0,2.0510580024,3.2816839976,-1.6440047127
 H,0,2.7931089596,2.1075448668,-0.5558141442
 H,0,3.3554812478,-3.0698681598,3.6466486919
 H,0,3.1940187437,-1.7385317291,4.8398703246
 H,0,1.7349259625,-2.4870911203,4.1533115596
```

```
dmallene+dmfumarate_2+2_ts2_1.log
 dmallene+dmfumarate 2+2 opt2 freq
ub3lyp/6-31g*
E(UB3LYP) = -729.545150265

Zero-point correction= 0.251827 (Hartree/Particle)
Thermal correction to Energy= 0.269600
Thermal correction to Enthalpy= 0.270545
Thermal correction to Gibbs Free Energy= 0.203689
Sum of electronic and ZPE= -729.293323
Sum of electronic and thermal Energies= -729.275550
Sum of electronic and thermal Enthalpies= -729.274606
Sum of electronic and thermal Free Energies= -729.341462

     E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 169.177 60.910 140.710
```

```
 C,0,2.32683845,-0.9676166869,1.7952711088
 C,0,1.2972244241,-1.4237107796,0.7982288354
 C,0,-0.1544496573,-1.2327489755,1.1337862443
 C,0,1.7083665618,-1.7769751005,-0.5540966092
 C,0,1.2884111908,-1.067744115,-1.8597621937
 C,0,2.3280616347,-0.1011951877,-2.3937718154
 O,0,3.3433770019,-0.7387799768,-3.0291142812
 C,0,4.3993044648,0.1127467982,-3.5043489856
 C,0,2.1978856913,-3.0133664261,-1.0251492127
 C,0,1.0888103823,-2.3691303933,-2.6343036049
 H,0,1.6813403692,-2.5593493135,-3.5223984742
 O,0,2.2973770192,1.0986960758,-2.2280291265
 H,0,3.0239969701,-3.0351073251,-1.7344670646
 H,0,2.1450239569,-3.906407167,-0.3954904819
```

```
 H,0,0.3641837044,-0.4994897356,-1.7161173545
 H,0,5.1099324272,-0.5501010937,-3.9990232509
 H,0,4.007859107,0.8521224443,-4.2076989851
 H,0,4.8756387536,0.634666029,-2.6700999986
 H,0,2.0829852135,-1.3253354636,2.8054332877
 H,0,3.3320088062,-1.3155690327,1.5372314194
 H,0,2.3668998876,0.13416247,1.8579743168
 H,0,-0.8059953463,-1.7464771024,0.4219447926
 H,0,-0.3728882085,-1.5918890342,2.1490717516
 H,0,-0.427576242,-0.162491863,1.1225206679
 C,0,-0.2408162684,-2.975564673,-2.5937666628
 O,0,-0.3490888813,-3.9970726193,-3.4874510948
 O,0,-1.1505351855,-2.6530467719,-1.8416843691
 C,0,-1.6064416828,-4.6835472394,-3.4751189776
 H,0,-1.5279343775,-5.4538212994,-4.2437009245
 H,0,-1.7923600703,-5.1374280369,-2.497084406
 H,0,-2.426742097,-3.9971564052,-3.7040075508
```

```
dmallene+dmfumarate_2+2_ts2_2.log
 dmallene+dmfumarate 2+2 opt2 freq
ub3lyp/6-31g*
E(UB3LYP) = -729.534695768

Zero-point correction= 0.251080 (Hartree/Particle)
Thermal correction to Energy= 0.268632
Thermal correction to Enthalpy= 0.269576
Thermal correction to Gibbs Free Energy= 0.204036
Sum of electronic and ZPE= -729.283616
Sum of electronic and thermal Energies= -729.266064
Sum of electronic and thermal Enthalpies= -729.265120
Sum of electronic and thermal Free Energies= -729.330660

      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 168.569 62.132 137.941
```

```
 H,0,2.3841074385,-1.4431352845,1.308679913
 C,0,1.4418494172,-1.5251713495,0.7696225416
 C,0,0.1875487858,-1.1135093032,1.3815637852
 C,0,-0.4812481672,0.1247701091,1.1454047118
 H,0,1.4511749122,-2.0506137204,-0.1846291831
 C,0,-0.9259453095,-2.1170737719,1.697949134
 C,0,-2.0029434364,-1.3831359997,0.9087493533
 C,0,-2.0747494607,-1.653532795,-0.5187430861
```

```
 O,0,-1.2296559761,-2.2525838796,-1.1736144317
 C,0,-1.1531836239,-2.4205132016,3.170843084
 O,0,-0.2896492223,-2.8377220044,3.9102412449
 O,0,-2.4279695821,-2.1953982305,3.5679814526
 C,0,-2.7036096122,-2.5059256181,4.9454805815
 O,0,-3.192801145,-1.1088650512,-1.0806811987
 C,0,-3.3058132549,-1.2875782409,-2.4966793474
 H,0,-2.9048863039,-1.0349480662,1.3975743266
 C,0,-1.2268294141,0.8641540503,2.2473333914
 C,0,0.0249404434,1.0413358859,0.0542425444
 H,0,-0.6754448366,-3.0802085431,1.2331199044
 H,0,-3.7591169467,-2.2745866625,5.0910245679
 H,0,-2.5088741071,-3.5628390237,5.1443239386
 H,0,-2.0799966254,-1.8999061331,5.6077866022
 H,0,-4.2422373833,-0.8047020463,-2.7805308978
 H,0,-2.4633872469,-0.8226941572,-3.0178484991
 H,0,-3.3311938693,-2.3503113577,-2.7549647797
 H,0,-2.0593490903,1.4476249023,1.8398818337
 H,0,-1.6128869841,0.2079801503,3.0289512193
 H,0,-0.5295114024,1.5727102836,2.7191122643
 H,0,0.4065580624,0.4770462991,-0.800766561
 H,0,-0.7769059471,1.7061971514,-0.2860914241
 H,0,0.8362368879,1.6813066085,0.4301920139
```

dmallene+dmfumarate 2+2 side opt
ub3lyp/6-31g*
E(UB3LYP) = -729.532977703

```
Zero-point correction= 0.247103 (Hartree/Particle)
Thermal correction to Energy= 0.265270
Thermal correction to Enthalpy= 0.266214
Thermal correction to Gibbs Free Energy= 0.198692
Sum of electronic and ZPE= -729.285875
Sum of electronic and thermal Energies= -729.267708
Sum of electronic and thermal Enthalpies= -729.266764
Sum of electronic and thermal Free Energies= -729.334286
```

```
      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 166.459 63.057 142.112
```

```
 C,0,0.9028533449,0.1907830154,0.6594488048
 O,0,-0.4692044299,0.0903800041,0.2503592542
 C,0,-1.2444058778,-0.7129396318,1.0261131877
```

```
 O,0,-0.8227986875,-1.3204237512,1.9910422506
 C,0,-2.6646825177,-0.6917841694,0.5762693146
 C,0,-2.9778594556,-0.2407799081,-0.7897362253
 H,0,-2.4464245695,-0.6672877233,-1.6365199063
 C,0,-3.5849578707,-1.7434982193,1.1903776015
 C,0,-3.7583654594,-3.0378830857,0.9030845618
 C,0,-2.970243062,-3.7499297755,-0.1655959273
 C,0,-4.2140406627,-0.8234224852,2.1853721027
 C,0,-4.7522873905,-3.8807299846,1.6617575589
 H,0,-3.3317485996,0.0917825115,1.4989113741
 H,0,1.3747577424,0.8585043435,-0.0623707093
 H,0,0.9743274217,0.6047954409,1.669101788
 H,0,1.3835029643,-0.7913347694,0.6462666696
 C,0,-4.0354555251,0.71132392,-1.0784004072
 H,0,-3.8681160359,-0.8701539474,3.2191407147
 H,0,-5.2260444216,-0.4550521596,2.0224883087
 H,0,-4.2474992437,-4.7092598266,2.1772514856
 H,0,-5.2986113004,-3.2979179735,2.4087334833
 H,0,-5.4831973654,-4.3346815543,0.9781190602
 H,0,-2.4191283352,-4.5976067088,0.2633181663
 H,0,-3.635794168,-4.1641841247,-0.9354793529
 H,0,-2.2469185696,-3.095021715,-0.6587504035
 O,0,-4.1541769462,0.9194621265,-2.418744745
 O,0,-4.7462921061,1.2659555108,-0.2504660133
 C,0,-5.1726712463,1.8524806149,-2.7991828581
 H,0,-5.1286983254,1.9073385654,-3.8876323066
 H,0,-6.1576955779,1.5061906472,-2.4725755542
 H,0,-4.9826197235,2.8352978134,-2.3579292783
```

dmallene+dmmaleate_side_Htransfer.log
dmallene+dmmaleate 2+2 side freq
ub3lyp/6-31g*
E(UB3LYP) = -729.532508630

Zero-point correction= 0.247247 (Hartree/Particle)
Thermal correction to Energy= 0.265369
Thermal correction to Enthalpy= 0.266313
Thermal correction to Gibbs Free Energy= 0.199476
Sum of electronic and ZPE= -729.285262
Sum of electronic and thermal Energies= -729.267140
Sum of electronic and thermal Enthalpies= -729.266195
Sum of electronic and thermal Free Energies= -729.333033

E CV S

```
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 166.522 63.035 140.671

 C,0,1.0054050331,0.2569432072,0.8931969588
 C,0,-0.4877584459,0.2909814374,0.5785757066
 C,0,-1.3085472318,-0.8921019282,0.9749981381
 O,0,-2.595448537,-0.7472112744,0.5745830886
 C,0,-3.464992198,-1.8333073169,0.9230701709
 C,0,-1.1052141146,1.6313384757,0.5276719775
 C,0,-1.9301936382,2.1416784487,1.6080425481
 O,0,-2.4027139532,3.3853329954,1.322962117
 C,0,-3.2427120812,3.9610886384,2.3313590337
 O,0,-2.1911088566,1.5500374568,2.6483017886
 O,0,-0.8795696935,-1.888669013,1.5208943018
 H,0,0.0077329373,0.0580951042,-0.6858356635
 H,0,-4.4440176829,-1.5629955565,0.5253807215
 H,0,-3.1140398612,-2.7685363118,0.477902355
 H,0,-3.5124714155,-1.9514444986,2.0089810911
 H,0,-3.5299157713,4.9415196421,1.9494166009
 H,0,-4.1277808767,3.3403578716,2.4985696024
 H,0,-2.7007031236,4.0609628794,3.2762884574
 H,0,-0.899698223,2.2950853121,-0.3066263148
 C,0,1.4450009403,0.0227371716,-0.5173397505
 C,0,1.6813877049,0.3709686736,2.0429451221
 H,0,1.7110773906,-0.9967214647,-0.8035875758
 H,0,1.935014376,0.8142100383,-1.0876645136
 C,0,3.1865325201,0.2754528188,2.0660120262
 C,0,1.0119546842,0.5564662614,3.378462788
 H,0,3.5104325162,-0.5715487591,2.6861656078
 H,0,3.6104062087,0.1460212961,1.0658507584
 H,0,3.6272709005,1.177148724,2.5133220216
 H,0,1.2332252763,-0.2998383314,4.0300649691
 H,0,1.4053639202,1.4473646455,3.8878148056
 H,0,-0.0723197045,0.6529623562,3.2999200611

dmallene.log
 dmallene 1
ub3lyp/6-31g*
E(UB3LYP) = -195.294208055

Zero-point correction= 0.112872 (Hartree/Particle)
Thermal correction to Energy= 0.119254
Thermal correction to Enthalpy= 0.120198
Thermal correction to Gibbs Free Energy= 0.083712
```

```
Sum of electronic and ZPE= -195.181336
Sum of electronic and thermal Energies= -195.174954
Sum of electronic and thermal Enthalpies= -195.174010
Sum of electronic and thermal Free Energies= -195.210496

     E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 74.833 22.093 76.792

 C,0,0.4952840577,0.0341109031,0.3804897105
 C,0,-0.1516903059,-0.4335295383,1.4168417068
 C,0,1.1440343685,0.5029043438,-0.6586715262
 H,0,-0.0774983014,-1.4782636652,1.7167766085
 H,0,-0.7940684331,0.2003419871,2.0271270159
 C,0,0.5346193174,0.4990660467,-2.0455083196
 C,0,2.5407201535,1.0758351518,-0.5326560617
 H,0,1.1575688217,-0.0801964434,-2.7407600618
 H,0,-0.4707995842,0.070321474,-2.0448165505
 H,0,0.4751966795,1.5205817436,-2.4454140602
 H,0,3.2456519442,0.5210791868,-1.1669166781
 H,0,2.5625093252,2.12121781,-0.8698011055
 H,0,2.9021079568,1.038715,0.4982183219

dmfumarate.log
 dmfumarate 1
ub3lyp/6-31g*
E(UB3LYP) = -534.345863993

Zero-point correction= 0.139387 (Hartree/Particle)
Thermal correction to Energy= 0.150409
Thermal correction to Enthalpy= 0.151353
Thermal correction to Gibbs Free Energy= 0.102146
Sum of electronic and ZPE= -534.206477
Sum of electronic and thermal Energies= -534.195455
Sum of electronic and thermal Enthalpies= -534.194510
Sum of electronic and thermal Free Energies= -534.243718

     E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 94.383 36.641 103.566

 C,0,-0.0767494937,0.,0.003141341
 C,0,0.0767494937,0.,1.331858659
 H,0,0.7845919452,0.,-0.6574996707
```

```
 C,0,1.4315271955,0.,1.941008126
 H,0,-0.7845919452,0.,1.9924996707
 C,0,-1.4315271955,0.,-0.606008126
 O,0,-1.3439514213,0.,-1.9541464991
 O,0,-2.4809045888,0.,0.005520976
 C,0,-2.6008866322,0.,-2.6497163125
 H,0,-2.3485155076,0.,-3.7101950975
 H,0,-3.1814268339,-0.8895787372,-2.39086323
 H,0,-3.1814268339,0.8895787372,-2.39086323
 O,0,1.3439514213,0.,3.2891464991
 O,0,2.4809045888,0.,1.329479024
 C,0,2.6008866322,0.,3.9847163125
 H,0,2.3485155076,0.,5.0451950975
 H,0,3.1814268339,-0.8895787372,3.72586323
 H,0,3.1814268339,0.8895787372,3.72586323

dmmaleate.log
 dmmaleate 1
ub3lyp/6-31g*
E(UB3LYP) = -534.335411423

Zero-point correction= 0.139128 (Hartree/Particle)
Thermal correction to Energy= 0.150126
Thermal correction to Enthalpy= 0.151070
Thermal correction to Gibbs Free Energy= 0.100951
Sum of electronic and ZPE= -534.196283
Sum of electronic and thermal Energies= -534.185286
Sum of electronic and thermal Enthalpies= -534.184341
Sum of electronic and thermal Free Energies= -534.234460

     E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 94.205 36.716 105.483

 C,0,-0.1689694379,3.8304756969,-0.6008465187
 O,0,0.0202547135,2.9100697353,0.4854390639
 C,0,-0.0264806411,1.6014963383,0.1467791963
 C,0,0.1666584913,0.7518367372,1.3483008414
 C,0,0.309634071,-0.5769172238,1.2881455339
 C,0,0.2766634883,-1.4087486929,0.0401839574
 O,0,1.3830470796,-1.2512483091,-0.7023139073
 C,0,1.3877377535,-1.9669832254,-1.9505214797
 O,0,-0.2174905988,1.2047034386,-0.9854305369
 O,0,-0.6233871576,-2.1810114345,-0.205812368
```

```
H,0,0.1647972561,1.2626779989,2.3062756058
H,0,0.3875597075,-1.1493136677,2.2097185061
H,0,-0.1132647413,4.8240530378,-0.1555430306
H,0,0.613622221,3.7011765847,-1.3533617306
H,0,-1.1429612667,3.6723141505,-1.0716601165
H,0,2.3682248335,-1.7800528749,-2.3887322228
H,0,1.2344984357,-3.0361295683,-1.783670136
H,0,0.5969257923,-1.5828227215,-2.5997056577
```

Part II

```
allene+tme_TS1_gas.log
 allene+tms_TSA1_2_gas ts
B3LYP/6-31G*
E(RB+HF-LYP) = -1555.39515493

Zero-point correction= 0.264758 (Hartree/Particle)
Thermal correction to Energy= 0.283650
Thermal correction to Enthalpy= 0.284595
Thermal correction to Gibbs Free Energy= 0.217780
Sum of electronic and ZPE= -1555.130397
Sum of electronic and thermal Energies= -1555.111505
Sum of electronic and thermal Enthalpies= -1555.110560
Sum of electronic and thermal Free Energies= -1555.177375

     E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 177.993 67.232 140.624

 C,0,0.0015698955,1.3835892126,3.476668398
 Al,0,-0.290955574,1.2133050048,1.5385067477
 Cl,0,1.4675769924,1.6852660456,0.3089498353
 C,0,-0.5365840375,-0.8475705518,1.1156021286
 C,0,-0.7339948507,-1.0583981815,-0.2799375453
 C,0,-1.5173110224,-0.5373422794,-1.2165050428
 Cl,0,-2.0627402185,2.2787891119,0.8204425352
 C,0,0.6347672287,-2.3093962688,-1.1492088572
 C,0,1.0136465745,-1.685179539,-2.4814166447
 C,0,-0.4113489506,-3.2266872676,-1.0084736741
 C,0,-1.348236338,-3.61017311,-2.122181356
 C,0,-0.5789860591,-4.0384018258,0.2485318295
 C,0,1.8132928985,-2.3131929448,-0.19300355
 H,0,-1.5483078095,-4.5441668053,0.2646175613
 H,0,-0.4977910862,-3.4202310471,1.1490381598
 H,0,0.2023176292,-4.807816687,0.3120346463
```

```
H,0,-1.1369420431,-4.6553448779,-2.3935626009
H,0,-2.3917140994,-3.5807261456,-1.7907362654
H,0,-1.2441581903,-3.0145445633,-3.0285484314
H,0,1.7674084776,-2.3189075884,-2.966971132
H,0,0.1854727388,-1.5659433829,-3.1794437192
H,0,1.460300962,-0.7009751014,-2.3147452553
H,0,2.6279368162,-2.8740323923,-0.669900639
H,0,1.6071649826,-2.7891565121,0.7650485075
H,0,2.1754779638,-1.2952414928,-0.0176032053
H,0,-1.6644183766,-0.9591239412,-2.2006676575
H,0,-2.0225646695,0.4019405855,-0.9931890898
H,0,0.4326669953,-1.1399601924,1.5203417477
H,0,-1.3462440674,-1.241942197,1.7388552829
H,0,0.185289212,2.4313128868,3.7461600361
H,0,-0.8705193498,1.0505249245,4.0543400519
H,0,0.8698703752,0.8053791235,3.819267198
```

allene+tme_TSA1_2_mpwpw91_631G.log
allene+tms_TSA1_2_phf_mpwpw91_1star opt
mpwpw91/6-31G*
E(RmPW+HF-PW91) = -1555.32058559

Zero-point correction= 0.270284 (Hartree/Particle)
Thermal correction to Energy= 0.289751
Thermal correction to Enthalpy= 0.290695
Thermal correction to Gibbs Free Energy= 0.221177
Sum of electronic and ZPE= -1555.050302
Sum of electronic and thermal Energies= -1555.030835
Sum of electronic and thermal Enthalpies= -1555.029891
Sum of electronic and thermal Free Energies= -1555.099409

```
     E      CV       S
  KCal/Mol Cal/Mol-K Cal/Mol-K
Total 181.821 67.179 146.313
```

```
C,0,-0.5488255959,-3.867584831,0.3095902459
C,0,-0.2656353986,-3.2149713077,-1.0075127848
C,0,0.9392410501,-2.6491898123,-1.323781212
C,0,2.1079346338,-2.6246202642,-0.3883582966
C,0,1.3199333363,-2.2091152777,-2.7051199945
C,0,-1.3583873889,-3.4683216713,-2.0018438883
H,0,-1.5543817143,-3.6229031027,0.6500827757
H,0,0.1522929654,-3.6165428463,1.0955975912
H,0,-0.5164926598,-4.9503042885,0.1763822935
```

```
 H,0,-1.4356240357,-4.5447013837,-2.1645025307
 H,0,-2.3181389244,-3.1390988567,-1.6071585345
 H,0,-1.2096236228,-3.0087407292,-2.9717318072
 H,0,2.0857288249,-2.8868407113,-3.0862886101
 H,0,0.5082831336,-2.2072033775,-3.4225320204
 H,0,1.7626914155,-1.214765096,-2.6817012735
 H,0,2.8083359353,-3.4067285869,-0.6865463824
 H,0,1.8561361293,-2.7930281511,0.651471273
 H,0,2.6413406194,-1.6779866583,-0.4663810939
 C,0,-0.4073636116,-0.9170528885,-0.3913254104
 C,0,-0.9561207192,-0.3986246683,-1.4527121723
 H,0,-0.9974483886,-0.8670585426,-2.4184957531
 H,0,-1.4023593624,0.5833700248,-1.3530216005
 C,0,-0.0890426788,-0.7760098373,0.9525721407
 H,0,0.972298978,-0.6793172507,1.170665516
 H,0,-0.583912432,-1.4746173225,1.6240899832
 Al,0,-0.8408640593,1.0396978291,1.6672315712
 Cl,0,-2.9938742204,0.9512803863,1.3719222724
 Cl,0,-0.0402228069,2.607316616,0.3889203209
 C,0,-0.2956363154,1.1913921648,3.5368766544
 H,0,-0.6779895407,2.1129540903,3.9782911728
 H,0,-0.6722740728,0.3621498703,4.1377544961
 H,0,0.7905455269,1.2079684807,3.6394990583
```

allene+tme_TSA_12shift_cdcl3.log
allene+tms_12shift_cdcl3 opt
B3LYP/6-31G*
E(RB3LYP) = -1555.41529945

Zero-point correction= 0.265843 (Hartree/Particle)
Thermal correction to Energy= 0.284400
Thermal correction to Enthalpy= 0.285344
Thermal correction to Gibbs Free Energy= 0.219186
Sum of electronic and ZPE= -1555.149456
Sum of electronic and thermal Energies= -1555.130899
Sum of electronic and thermal Enthalpies= -1555.129955
Sum of electronic and thermal Free Energies= -1555.196113

```
     E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 178.464 66.637 139.242
```

```
 C,0,0.6553059394,-0.5824978839,0.7178982633
 Al,0,-0.5582200043,0.7126160922,1.7122963782
```

```
 Cl,0,0.3143162729,0.7687103194,3.7557924854
 C,0,0.2327420244,-0.9916426609,-0.6573500733
 C,0,-0.2317140676,-0.1198552101,-1.578020271
 C,0,-0.7607873535,2.54313916,0.9910753872
 H,0,-1.2855664988,3.1826231163,1.7133451851
 Cl,0,-2.5561727825,-0.2731041233,1.8649932379
 C,0,0.8772533944,-2.482349878,-1.3747021187
 C,0,2.1186240984,-2.9159974168,-0.6111355427
 C,0,-0.4421806523,-2.7225965442,-0.8809707282
 C,0,-0.7156461196,-3.324910162,0.4767484225
 C,0,1.1642550646,-2.4132739215,-2.8683755599
 C,0,-1.6579338529,-2.8026202483,-1.7802148779
 H,0,-0.3380743911,0.928762832,-1.3132629017
 H,0,-0.4875998959,-0.3789013905,-2.5962906
 H,0,1.6506666352,-0.1201660471,0.6546811324
 H,0,0.7661174236,-1.4304961706,1.3949053337
 H,0,0.2113649141,3.0159967296,0.7933904471
 H,0,-1.3403365536,2.5845963756,0.058565977
 H,0,-1.4804175144,-2.7511063219,1.0091868717
 H,0,-1.1243335393,-4.3269186172,0.2936263849
 H,0,0.1600315419,-3.4382234199,1.1111790339
 H,0,-2.54653908,-2.4496145066,-1.250867333
 H,0,-1.5728096166,-2.2675967894,-2.7231351155
 H,0,-1.8108445055,-3.8639397733,-2.0155048638
 H,0,1.473176431,-3.41595827,-3.1885163673
 H,0,0.3169752061,-2.1248269793,-3.4876263854
 H,0,1.9942221811,-1.7303914626,-3.0674420196
 H,0,2.3359270248,-3.9537211706,-0.8919969875
 H,0,2.9731327736,-2.3029152261,-0.9100819762
 H,0,2.0266985024,-2.8692674309,0.4707901815
```

allene+tme_TSA_2.2A_cdcl3.log
allene+tms_tsA1_2.2A_cdcl3 opt
B3LYP/6-31G*
E(RB3LYP) = -1555.41175418

Zero-point correction= 0.263784 (Hartree/Particle)
Thermal correction to Energy= 0.283325
Thermal correction to Enthalpy= 0.284269
Thermal correction to Gibbs Free Energy= 0.214570
Sum of electronic and ZPE= -1555.147971
Sum of electronic and thermal Energies= -1555.128429
Sum of electronic and thermal Enthalpies= -1555.127485
Sum of electronic and thermal Free Energies= -1555.197184

```
      E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 177.789 67.853 146.693

 C,0,-0.1199983048,-0.8377615822,0.975463584
 Al,0,-0.6113330482,1.0772410815,1.6264150697
 Cl,0,-0.1899212211,0.9091685404,3.7866578902
 C,0,-0.4120807398,-1.0576118921,-0.4044084397
 C,0,-1.0946120051,-0.4831000131,-1.3791989587
 C,0,0.4177532766,2.5147213525,0.7600436153
 H,0,0.1581795254,3.4927927423,1.1853927743
 Cl,0,-2.7924137975,1.3160650342,1.3658251977
 C,0,0.8943849883,-2.5495745097,-1.3168135692
 C,0,2.1022259564,-2.5816372949,-0.408908119
 C,0,-0.2809201083,-3.2380294953,-1.0213803836
 C,0,-0.4881971739,-3.9777359199,0.2754794178
 C,0,1.2482511997,-2.0724215967,-2.7093908377
 C,0,-1.3442545152,-3.5529625225,-2.0440305619
 H,0,-1.5847767319,0.4677065507,-1.1769820435
 H,0,-1.2200318268,-0.8884797086,-2.3728558018
 H,0,0.9470046308,-0.872200595,1.218384213
 H,0,-0.6660021666,-1.5073476614,1.6487318795
 H,0,1.4984008262,2.3783130317,0.9010065291
 H,0,0.2333166162,2.5734561395,-0.3206442618
 H,0,-1.5499162818,-4.0064663534,0.5386876161
 H,0,-0.1601600818,-5.0168862787,0.1354205625
 H,0,0.0683689321,-3.5701679396,1.1181287882
 H,0,-2.3414789646,-3.333013582,-1.6505119514
 H,0,-1.2221733483,-3.0515011402,-3.0029454837
 H,0,-1.311057394,-4.6342386231,-2.23634264
 H,0,1.9034058711,-2.8219294976,-3.1730409397
 H,0,0.3988980665,-1.9296790892,-3.3756922506
 H,0,1.8111017649,-1.1356884449,-2.6619647535
 H,0,2.8019607755,-3.3277186837,-0.8082364035
 H,0,2.6226855567,-1.618622262,-0.4184337732
 H,0,1.8876517231,-2.8549817869,0.6226210349
allene+tms_TSA_syn.log
 allene+tms_tsA1 opt
B3LYP/6-31G*
E(RB+HF-LYP) = -1594.70397187

Zero-point correction= 0.295172 (Hartree/Particle)
Thermal correction to Energy= 0.314957
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```
Thermal correction to Enthalpy= 0.315901
Thermal correction to Gibbs Free Energy= 0.246787
Sum of electronic and ZPE= -1594.408800
Sum of electronic and thermal Energies= -1594.389015
Sum of electronic and thermal Enthalpies= -1594.388071
Sum of electronic and thermal Free Energies= -1594.457185

      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 197.638 70.978 145.462

 C,0,0.2793540918,0.2985990211,-0.2076262794
 C,0,0.1982255744,-0.3229599117,1.0890885022
 C,0,1.8187521379,-0.208462583,0.4478316327
 C,0,2.5133445178,-1.4424387017,-0.0256993172
 Al,0,3.492449106,-2.5191184425,1.4492984356
 C,0,5.3318743565,-3.0090649311,0.9010072985
 C,0,2.5365761234,0.8214779912,0.9841717061
 Cl,0,3.4879999611,-1.1284534827,3.2006093649
 Cl,0,2.2460327803,-4.2659181503,1.9341753811
 C,0,0.077981859,1.7944222811,-0.406603432
 C,0,-0.0560683061,0.462241481,2.3671930337
 C,0,-0.232900902,-1.7684169004,1.2612518525
 C,0,-0.0400219769,-0.4564821816,-1.486279386
 H,0,3.6186459429,0.7593594753,1.0260022094
 H,0,2.1008635513,1.7327867911,1.3696262762
 H,0,3.3003103327,-1.1472799543,-0.7324322424
 H,0,1.8656935428,-2.137013679,-0.5605225225
 C,0,6.1619884389,-3.7853413791,1.9401767613
 H,0,5.2638578551,-3.6012925022,-0.0260107512
 H,0,5.8706242632,-2.090161612,0.616679511
 H,0,7.1661708472,-4.0388344836,1.5702475642
 H,0,6.2921652064,-3.204401617,2.8613120717
 H,0,5.6717931496,-4.725581518,2.2196157828
 H,0,0.1900889481,-2.1918747806,2.1743278063
 H,0,-1.3269581197,-1.7669959746,1.3590849604
 H,0,0.0303434247,-2.4319806715,0.4420221928
 H,0,0.5459783395,0.0483109474,3.1807940086
 H,0,0.1390716797,1.5316227374,2.2971698437
 H,0,-1.1140839854,0.3389957737,2.6300893117
 H,0,-0.9810002545,1.9593689481,-0.6444847978
 H,0,0.3114565949,2.4079579643,0.4612142239
 H,0,0.6665824142,2.1533694689,-1.255984204
 H,0,-1.0835707142,-0.2380781035,-1.7476591542
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 H,0,0.5890379218,-0.1014378931,-2.3080954539
 H,0,0.0654592975,-1.535295427,-1.4117881906

allene+TSA1_2_cdcl3_m06_freq.log
 allene+tms_TSA1_2_chcl3_m06 ts
m06/6-31G*
E(RM06) = -1555.00130006

Zero-point correction= 0.261415 (Hartree/Particle)
Thermal correction to Energy= 0.281065
Thermal correction to Enthalpy= 0.282009
Thermal correction to Gibbs Free Energy= 0.212587
Sum of electronic and ZPE= -1554.739885
Sum of electronic and thermal Energies= -1554.720235
Sum of electronic and thermal Enthalpies= -1554.719291
Sum of electronic and thermal Free Energies= -1554.788713

     E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 176.371 68.564 146.111

 C,0,-0.2134857728,1.2866486355,3.5429676474
 Al,0,-0.5018074696,1.1729747505,1.6167801531
 Cl,0,1.0975336523,2.0596103634,0.4121836844
 C,0,-0.4207956189,-0.8242768491,1.0690035283
 C,0,-0.6657859186,-0.9779687728,-0.3079722335
 C,0,-1.2738062091,-0.4194697118,-1.3292259662
 Cl,0,-2.4130322898,2.0202081136,0.9691867886
 C,0,0.7700039934,-2.4679125462,-1.2440216893
 C,0,1.1019298189,-1.9321587861,-2.6047914341
 C,0,-0.3860465101,-3.1611567722,-0.9481594684
 C,0,-1.4407536559,-3.4947484115,-1.9605405091
 C,0,-0.6073245252,-3.8768107029,0.3487845778
 C,0,1.9443567947,-2.3779459433,-0.3192451301
 H,0,-1.6653511008,-3.8241062539,0.6379099323
 H,0,-0.0073137201,-3.5072468344,1.1830232629
 H,0,-0.367942952,-4.9415938174,0.2137030783
 H,0,-1.4373367843,-4.5834182786,-2.1167853639
 H,0,-2.4387860336,-3.2377481948,-1.5827719898
 H,0,-1.3077596821,-3.0292330693,-2.9396486264
 H,0,1.8824641268,-2.5639917787,-3.0520547273
 H,0,0.2684264221,-1.9006399943,-3.3093159447
 H,0,1.5197816302,-0.9202141959,-2.5197996167
 H,0,2.777976294,-2.9386729446,-0.7648522361
```

H,0,1.7802325389,-2.7823615825,0.6815832719
H,0,2.2859127309,-1.3364357221,-0.2305273705
H,0,-1.3665403743,-0.8510723366,-2.3189312488
H,0,-1.7301449875,0.5607114706,-1.1671255102
H,0,0.6209717343,-0.9815888656,1.3778728062
H,0,-1.1024687554,-1.3883717752,1.7187163384
H,0,-0.182258977,2.3306373912,3.8808944457
H,0,-1.0158690758,0.7850911613,4.1007555615
H,0,0.7369636766,0.8189142535,3.8347139883

allene+TSA1_2_mpwpw91_phf_1star.log
allene+tms_TSA1_2_phf_mpwpw91_1star opt
mpwpw91/6-31+G*
E(RmPW+HF-PW91) = -1555.32847672

Zero-point correction= 0.269548 (Hartree/Particle)
Thermal correction to Energy= 0.289132
Thermal correction to Enthalpy= 0.290076
Thermal correction to Gibbs Free Energy= 0.220076
Sum of electronic and ZPE= -1555.058929
Sum of electronic and thermal Energies= -1555.039345
Sum of electronic and thermal Enthalpies= -1555.038401
Sum of electronic and thermal Free Energies= -1555.108401

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 181.433 67.373 147.327

C,0,-0.5467829914,-3.8695618601,0.3092347774
C,0,-0.2649890044,-3.2171066868,-1.0081993588
C,0,0.9394162598,-2.6493586293,-1.3246242307
C,0,2.1078729786,-2.6238069715,-0.3890011999
C,0,1.3194582329,-2.210887786,-2.706666356
C,0,-1.3559759571,-3.4739950484,-2.0035314654
H,0,-1.5544465348,-3.6303874353,0.6482388869
H,0,0.1515536695,-3.6140989236,1.0964392698
H,0,-0.5082789273,-4.952755158,0.1779345829
H,0,-1.4284967759,-4.5508647769,-2.1678152233
H,0,-2.3181438236,-3.1502529081,-1.6093768419
H,0,-1.2093916595,-3.0128131004,-2.9730889376
H,0,2.0813758265,-2.8923722031,-3.0900977796
H,0,0.5067262273,-2.2042386552,-3.4229277513
H,0,1.767743863,-1.2186894947,-2.6845303149
H,0,2.8085143309,-3.406880534,-0.6857240018

```
 H,0,1.8564303192,-2.7908894983,0.6512556382
 H,0,2.6423622229,-1.6775755371,-0.4681152894
 C,0,-0.4119018974,-0.9135488255,-0.3925936059
 C,0,-0.9638667855,-0.3976827141,-1.4541065947
 H,0,-1.0058023564,-0.8680002296,-2.4193676704
 H,0,-1.4135183865,0.5832900226,-1.3556683948
 C,0,-0.0914873104,-0.7714725367,0.950586012
 H,0,0.9707782935,-0.6752446816,1.1660975193
 H,0,-0.5850781654,-1.4707607037,1.6228504577
 Al,0,-0.8362159323,1.0449885655,1.6701955016
 Cl,0,-2.9889501829,0.9725955666,1.3714207635
 Cl,0,-0.0270662467,2.6129415199,0.3987448306
 C,0,-0.2956156255,1.1907207423,3.5430676035
 H,0,-0.6771497388,2.1146334026,3.9820390492
 H,0,-0.6794746532,0.3617660577,4.1408432727
 H,0,0.7909457311,1.2031110208,3.6484208513
```

allene+TSA1_2_mpwpw91_phf.log
 allene+tms_TSA1_2_mpwpw91_phf ts
mpwpw91/6-31+G**
E(RmPW+HF-PW91) = -1555.35613373

Zero-point correction= 0.268211 (Hartree/Particle)
Thermal correction to Energy= 0.287814
Thermal correction to Enthalpy= 0.288758
Thermal correction to Gibbs Free Energy= 0.218854
Sum of electronic and ZPE= -1555.087923
Sum of electronic and thermal Energies= -1555.068320
Sum of electronic and thermal Enthalpies= -1555.067376
Sum of electronic and thermal Free Energies= -1555.137280

```
      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 180.606 67.637 147.125
```

```
 C,0,-0.5444816866,-3.8682984818,0.3105166854
 C,0,-0.264786616,-3.2166646488,-1.0071468944
 C,0,0.9399948279,-2.6499218543,-1.3244632387
 C,0,2.1075781121,-2.6249680207,-0.3886611484
 C,0,1.3173386912,-2.2135783519,-2.7073113124
 C,0,-1.3546127295,-3.4720525399,-2.0033065154
 H,0,-1.5511723228,-3.6289520204,0.649881865
 H,0,0.1555977105,-3.6115521098,1.0948512862
 H,0,-0.5057783994,-4.9504941318,0.1787884171
```

```
H,0,-1.4209114205,-4.5474015371,-2.1742143875
H,0,-2.3171548386,-3.1557042985,-1.6062171538
H,0,-1.2089569441,-3.0035962351,-2.9687288867
H,0,2.0694937333,-2.9024945051,-3.0942411145
H,0,0.5006521192,-2.1990069029,-3.4178620124
H,0,1.7754948154,-1.226743632,-2.6856030884
H,0,2.8086683525,-3.4053351782,-0.6879750273
H,0,1.8545290326,-2.7959426939,0.6498704098
H,0,2.6394282534,-1.6778922558,-0.4654786483
C,0,-0.4115753151,-0.9114639067,-0.3927661574
C,0,-0.9617051395,-0.3942674855,-1.4540029661
H,0,-1.0035794707,-0.8643223065,-2.4187640548
H,0,-1.4076100449,0.5874736844,-1.350182311
C,0,-0.0919768707,-0.7720771307,0.9503560374
H,0,0.9693721279,-0.6744216435,1.1662779999
H,0,-0.5895006507,-1.4692330509,1.6208862013
Al,0,-0.8368056409,1.0421843765,1.6713186357
Cl,0,-2.9896824829,0.9669607379,1.3734767506
Cl,0,-0.031640755,2.6112479843,0.3984634376
C,0,-0.2961506911,1.190289904,3.5425781161
H,0,-0.6811346958,2.1128160534,3.9787236473
H,0,-0.6779733342,0.3601967329,4.1381152651
H,0,0.789589273,1.2060154485,3.6447531632
```

allene+TSA1_2_phf.log
allene+tms_TSA1_2_phf opt
B3LYP/6-31G*
E(RB3LYP) = -1555.41319976

Zero-point correction= 0.263724 (Hartree/Particle)
Thermal correction to Energy= 0.283278
Thermal correction to Enthalpy= 0.284223
Thermal correction to Gibbs Free Energy= 0.214465
Sum of electronic and ZPE= -1555.149475
Sum of electronic and thermal Energies= -1555.129921
Sum of electronic and thermal Enthalpies= -1555.128977
Sum of electronic and thermal Free Energies= -1555.198735

```
     E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 177.760 67.909 146.818
```

```
C,0,-0.4805922453,-3.9018331086,0.3405224315
C,0,-0.2793458346,-3.1937598941,-0.976833252
```

C,0,0.9154884181,-2.5655371468,-1.3231724031
C,0,2.1252786764,-2.5483496453,-0.4205186007
C,0,1.2587561027,-2.1502975209,-2.7356984557
C,0,-1.3646455848,-3.5281141643,-1.9739165033
H,0,-1.5193825064,-3.8104203335,0.6734989683
H,0,0.1734647562,-3.5619323272,1.1412934021
H,0,-0.2855831783,-4.971500807,0.1852766973
H,0,-1.309911749,-4.6051014937,-2.1832851617
H,0,-2.3537465106,-3.3345180084,-1.5483039878
H,0,-1.2868892247,-3.0101259298,-2.9284057183
H,0,1.9608429556,-2.8892575812,-3.1446666205
H,0,0.4121720079,-2.0989329106,-3.4183586307
H,0,1.7705991128,-1.1834778337,-2.7394788173
H,0,2.8161153119,-3.3286257012,-0.7666170604
H,0,1.9118367407,-2.7435520464,0.628506145
H,0,2.6554636886,-1.5938526963,-0.5015971594
C,0,-0.4192456948,-1.038745898,-0.4359043892
C,0,-1.0259844577,-0.4487573682,-1.4497818952
H,0,-1.114501035,-0.8574669744,-2.4459195956
H,0,-1.4835747735,0.5239290492,-1.2796442786
C,0,-0.1609035693,-0.7994680344,0.9494846804
H,0,0.9039988209,-0.8137015042,1.2072647616
H,0,-0.699212588,-1.4836711223,1.6156465321
Al,0,-0.7090491608,1.0794467949,1.6376465462
Cl,0,-2.8386700141,1.4029956799,1.1389268747
Cl,0,0.4794600269,2.5430652221,0.4842893956
C,0,-0.3688207459,1.1713912429,3.5746561052
H,0,-0.6198576389,2.1622995769,3.9743887732
H,0,-0.9689599077,0.4366793626,4.1278964528
H,0,0.6859448009,0.9819951219,3.8147387636

allene+tme_TSB1_temp.log
allene+tme_TSC1_desynallene_cdcl3 opt
B3LYP/6-31G*
E(RB3LYP) = -1555.41469928

C,0,-1.5148556852,-1.0789194567,0.9597231003
C,0,-0.6507411833,-2.1065966361,0.8006870821
C,0,0.6680893279,-1.6457557894,0.9418636796
Al,0,-1.2247349031,-4.2695937939,0.4851372119
Cl,0,-0.0711925502,-4.8769203808,-1.2838511309
Cl,0,-0.3785747618,-5.2344585242,2.2650006345
C,0,-3.1651969603,-4.4598076268,0.2730479694

```
 H,0,-3.4387107098,-5.5031209684,0.0696745009
 C,0,-0.0289006315,0.1882458411,-0.053305064
 C,0,-1.2277798361,0.6557218576,-0.899800586
 C,0,0.0468868892,0.4345170268,1.2953899083
 C,0,-0.9355151559,1.3366123947,2.0584737961
 C,0,1.167037057,0.1491667962,-0.9997871925
 C,0,1.4249357323,0.6653973105,1.9671330718
 H,0,1.2722399263,-2.0867791804,1.7535826926
 H,0,1.3024158462,-1.5234971483,0.0868568451
 H,0,-2.5714796025,-1.2308207914,0.6803833657
 H,0,-1.4571260433,-0.4940916547,1.8413460325
 H,0,-3.7028855335,-4.148946832,1.1776523498
 H,0,-3.5426939071,-3.8556910186,-0.5622399785
 H,0,1.3773689974,0.3688772459,3.0203832768
 H,0,2.2586060265,0.125120428,1.51887746
 H,0,1.6694497791,1.7356541835,1.9460722108
 H,0,-1.0584352098,1.0099792381,3.0976943441
 H,0,-0.4917105996,2.3389837544,2.0938025812
 H,0,-1.9223043243,1.4238173554,1.6025597038
 H,0,1.1546007473,1.0831380281,-1.5727056659
 H,0,2.1399779672,0.077872504,-0.514967604
 H,0,1.0670949913,-0.6634761023,-1.7292923432
 H,0,-1.4186514193,-0.0427160187,-1.7203039692
 H,0,-2.1577161207,0.7860977843,-0.3492210365
 H,0,-0.9685511505,1.6242421741,-1.3491522466
```

```
g03.log
 tme+AlEtCl2 opt
B3LYP/6-31G*
E(RB+HF-LYP) = -1478.07046161

Zero-point correction= 0.235506 (Hartree/Particle)
Thermal correction to Energy= 0.252900
Thermal correction to Enthalpy= 0.253845
Thermal correction to Gibbs Free Energy= 0.188019
Sum of electronic and ZPE= -1477.834956
Sum of electronic and thermal Energies= -1477.817561
Sum of electronic and thermal Enthalpies= -1477.816617
Sum of electronic and thermal Free Energies= -1477.882442

      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 158.697 58.392 138.541
```

```
 C,0,1.3735711028,0.0676620989,-0.7640607906
 C,0,0.0659871527,0.2091546303,-0.0124297069
 C,0,-1.1345571457,-0.0476496689,-0.8986253761
 C,0,-0.0276616388,0.3145768151,1.3504347999
 C,0,-1.3503209295,0.1789965821,2.084655146
 C,0,1.1671333433,0.2593128288,2.2834780268
 Al,0,0.1066028453,2.8996065333,0.6132297838
 C,0,1.9770633814,3.2931295697,0.1473245863
 C,0,2.2617202787,4.8111630179,0.182830197
 Cl,0,-1.4139487891,3.3142898826,-0.8468454887
 Cl,0,-0.5111859474,3.4725192297,2.5942886893
 H,0,2.6552187896,2.7795746137,0.8427532034
 H,0,2.2079690783,2.902358002,-0.8517551534
 H,0,3.3066521677,5.02971795,-0.0740989154
 H,0,1.6324903237,5.3571478232,-0.5302524001
 H,0,2.074729563,5.2356181721,1.1759422375
 H,0,1.0707257282,0.9991021342,3.084225081
 H,0,1.1870358185,-0.7287506581,2.7649673876
 H,0,2.1299749165,0.4057462162,1.7930851949
 H,0,1.3633191913,0.6701005897,-1.678749016
 H,0,2.2585869734,0.3377242165,-0.1890138529
 H,0,1.4849283309,-0.9792000065,-1.0802530709
 H,0,-1.0353587389,0.4710733289,-1.8561376719
 H,0,-1.181241364,-1.1252638068,-1.1141437015
 H,0,-2.086318572,0.2457112536,-0.4574200458
 H,0,-1.3084285033,0.6840477997,3.0521802284
 H,0,-2.2028440551,0.5846243203,1.5370191662
 H,0,-1.5507103015,-0.8856254683,2.2719594624
g09.log
 AlMeCl2 freq ts
B3LYP/6-31G*
E(RB3LYP) = -1202.89837612

Zero-point correction= 0.038958 (Hartree/Particle)
Thermal correction to Energy= 0.045429
Thermal correction to Enthalpy= 0.046373
Thermal correction to Gibbs Free Energy= 0.006214
Sum of electronic and ZPE= -1202.859418
Sum of electronic and thermal Energies= -1202.852947
Sum of electronic and thermal Enthalpies= -1202.852003
Sum of electronic and thermal Free Energies= -1202.892162

     E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
```

```
Total 28.507 19.029 84.522

 Al,0,0.0802724576,0.,-0.2734518553
 Cl,0,-0.3034689984,0.,1.8137175746
 Cl,0,2.1386070159,0.,-0.7921809772
 C,0,-1.3213793713,0.,-1.6126207402
 H,0,-2.3143296401,0.,-1.1525295741
 H,0,-1.2345037316,0.8841256818,-2.2547977137
 H,0,-1.2345037316,-0.8841256818,-2.2547977137

g09.log
 allene+AlMeCl2_freq
B3LYP/6-31G*
E(RB3LYP) = -1319.57043842

Zero-point correction= 0.095800 (Hartree/Particle)
Thermal correction to Energy= 0.106323
Thermal correction to Enthalpy= 0.107267
Thermal correction to Gibbs Free Energy= 0.058794
Sum of electronic and ZPE= -1319.474639
Sum of electronic and thermal Energies= -1319.464116
Sum of electronic and thermal Enthalpies= -1319.463172
Sum of electronic and thermal Free Energies= -1319.511645

      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 66.718 34.289 102.020

6 -2.023802 0.071642 1.689893
13 -0.702989 0.037008 0.246951
17 -0.873349 -1.564246 -1.205930
6 1.278265 -0.583684 1.547670
6 2.194113 -0.350978 0.608122
6 3.044797 -0.068612 -0.327519
17 -0.294402 1.931736 -0.728122
1 2.722197 0.363631 -1.272115
1 4.105081 -0.265708 -0.184575
1 0.936349 -1.605021 1.727428
1 1.165874 0.122824 2.371851
1 -3.017227 0.281105 1.273660
1 -2.080121 -0.888376 2.216760
1 -1.801767 0.852911 2.426521

allene_chcl3_freq.log
```

```
 allene_chcl3 opt
B3LYP/6-31G*
E(RB3LYP) = -116.658832521

Zero-point correction= 0.055398 (Hartree/Particle)
Thermal correction to Energy= 0.059156
Thermal correction to Enthalpy= 0.060100
Thermal correction to Gibbs Free Energy= 0.031308
Sum of electronic and ZPE= -116.603434
Sum of electronic and thermal Energies= -116.599676
Sum of electronic and thermal Enthalpies= -116.598732
Sum of electronic and thermal Free Energies= -116.627525

     E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 37.121 11.705 60.599

 C,0,0.0000001197,-0.0102936678,1.2282882474
 C,0,0.0000003466,0.0124367125,-0.0793290666
 C,0,0.0000005493,0.0343567668,-1.3866242581
 H,0,0.9270183739,-0.019729256,1.798742192
 H,0,-0.9270183404,-0.0197315217,1.7987418247
 H,0,0.0000037153,-0.8837742142,-1.971251975
 H,0,0.0000045608,0.9703521804,-1.9420669645

allene_phf_freq.log
 allene_phf opt
B3LYP/6-31G*
E(RB3LYP) = -116.658896674

Zero-point correction= 0.055405 (Hartree/Particle)
Thermal correction to Energy= 0.059163
Thermal correction to Enthalpy= 0.060107
Thermal correction to Gibbs Free Energy= 0.031315
Sum of electronic and ZPE= -116.603491
Sum of electronic and thermal Energies= -116.599734
Sum of electronic and thermal Enthalpies= -116.598790
Sum of electronic and thermal Free Energies= -116.627582

     E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 37.125 11.702 60.598

 C,0,0.0131818938,0.011127129,-0.009324104
```

```
 C,0,0.002501364,-0.0101363216,1.2980051624
 C,0,0.0232143396,0.0322783898,-1.3166635525
 H,0,0.9252443909,-0.0178519521,1.8752439333
 H,0,-0.9295280644,-0.0209036171,1.8601105306
 H,0,0.02939346,-0.8859368781,-1.9012908512
 H,0,0.0260456162,0.9688212501,-1.8712961185
```

```
tme_chcl3_freq.log
 tme_chcl3 opt
B3LYP/6-31G*
E(RB3LYP) = -235.852026509

Zero-point correction= 0.162981 (Hartree/Particle)
Thermal correction to Energy= 0.168799
Thermal correction to Enthalpy= 0.169743
Thermal correction to Gibbs Free Energy= 0.135024
Sum of electronic and ZPE= -235.689046
Sum of electronic and thermal Energies= -235.683227
Sum of electronic and thermal Enthalpies= -235.682283
Sum of electronic and thermal Free Energies= -235.717003

      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 105.923 21.751 73.074

 C,0,0.,0.,-0.0075553142
 C,0,0.,0.,1.3425553142
 C,0,1.2994230304,0.,-0.7863442902
 C,0,1.2994230304,0.,2.1213442902
 C,0,-1.2994230304,0.,2.1213442902
 C,0,-1.2994230304,0.,-0.7863442902
 H,0,-1.1240580169,0.,-1.866919183
 H,0,-1.9186200075,-0.8788168301,-0.5564841743
 H,0,-1.9186200075,0.8788168301,-0.5564841743
 H,0,1.1240580169,0.,-1.866919183
 H,0,1.9186200075,0.8788168301,-0.5564841743
 H,0,1.9186200075,-0.8788168301,-0.5564841743
 H,0,-1.1240580169,0.,3.201919183
 H,0,-1.9186200075,0.8788168301,1.8914841743
 H,0,-1.9186200075,-0.8788168301,1.8914841743
 H,0,1.1240580169,0.,3.201919183
 H,0,1.9186200075,-0.8788168301,1.8914841743
 H,0,1.9186200075,0.8788168301,1.8914841743
```

```
tme_phf_freq.log
 tme_phf opt
B3LYP/6-31G*
E(RB3LYP) = -235.852057914

Zero-point correction= 0.162967 (Hartree/Particle)
Thermal correction to Energy= 0.168786
Thermal correction to Enthalpy= 0.169730
Thermal correction to Gibbs Free Energy= 0.135010
Sum of electronic and ZPE= -235.689091
Sum of electronic and thermal Energies= -235.683272
Sum of electronic and thermal Enthalpies= -235.682328
Sum of electronic and thermal Free Energies= -235.717048

      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 105.915 21.754 73.075

 C,0,0.,0.,-0.0075687703
 C,0,0.,0.,1.3425687703
 C,0,1.2994425078,0.,-0.7863765593
 C,0,1.2994425078,0.,2.1213765593
 C,0,-1.2994425078,0.,2.1213765593
 C,0,-1.2994425078,0.,-0.7863765593
 H,0,-1.1240434847,0.,-1.8669446725
 H,0,-1.9186607511,-0.8787986553,-0.5564944036
 H,0,-1.9186607511,0.8787986553,-0.5564944036
 H,0,1.1240434847,0.,-1.8669446725
 H,0,1.9186607511,0.8787986553,-0.5564944036
 H,0,1.9186607511,-0.8787986553,-0.5564944036
 H,0,-1.1240434847,0.,3.2019446725
 H,0,-1.9186607511,0.8787986553,1.8914944036
 H,0,-1.9186607511,-0.8787986553,1.8914944036
 H,0,1.1240434847,0.,3.2019446725
 H,0,1.9186607511,-0.8787986553,1.8914944036
 H,0,1.9186607511,0.8787986553,1.8914944036

allene+dedm_dich_TS1_A.log
 allene+dedm_TSA__dich_1 opt
B3LYP/6-31G*
E(RB3LYP) = -1634.03875190

Zero-point correction= 0.321528 (Hartree/Particle)
Thermal correction to Energy= 0.343572
```

```
Thermal correction to Enthalpy= 0.344516
Thermal correction to Gibbs Free Energy= 0.268529
Sum of electronic and ZPE= -1633.717224
Sum of electronic and thermal Energies= -1633.695180
Sum of electronic and thermal Enthalpies= -1633.694236
Sum of electronic and thermal Free Energies= -1633.77022

     E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 215.595 77.497 159.928
```

```
 C,0,-3.1195196531,0.3143789325,2.124760673
 Al,0,-2.1905637116,0.40334294,0.3924879639
 Cl,0,-2.7196458279,2.2057823174,-0.7715905023
 Cl,0,0.0097663454,0.3647205317,0.5901632922
 C,0,-2.7269842948,-1.2610351377,-0.7375305825
 C,0,-2.1224923685,-1.3020528836,-2.0202160933
 C,0,-1.3816748543,-0.5824137941,-2.8370747707
 C,0,-1.9942263856,-3.435786546,-2.8289597064
 C,0,-1.9992205513,-4.2659761771,-1.5658320479
 C,0,-0.6829397202,-3.573390266,-3.571518388
 C,0,-3.1463885694,-2.8919525559,-3.3906591058
 C,0,-4.5061381661,-3.0563453389,-2.7432945659
 C,0,-5.2810965987,-4.2503104939,-3.3398981105
 C,0,-3.1777592648,-2.3793830335,-4.8220073402
 H,0,-3.4624833825,-3.2411586989,-5.4455641665
 H,0,-5.0915153491,-2.1424802859,-2.8855112979
 H,0,-4.4198542961,-3.2005391236,-1.6663590393
 C,0,-4.1362331183,-1.2166571706,-5.1183829207
 H,0,-2.1781651853,-2.1091877974,-5.1644089064
 H,0,-0.6086604161,-4.604149951,-3.9440037626
 H,0,-0.563210913,-2.914757081,-4.4301487417
 H,0,0.160897503,-3.4158740796,-2.8929672322
 H,0,-1.915902132,-5.3227659202,-1.8522199454
 H,0,-2.8934265724,-4.1640961589,-0.9536197543
 H,0,-1.1231126413,-4.0364339826,-0.9498999365
 H,0,-1.082016042,-0.8782966911,-3.8319574218
 H,0,-1.034498954,0.3902279572,-2.4916976605
 H,0,-2.4226342737,-2.0756248005,-0.0716315635
 H,0,-3.8205512021,-1.1964856708,-0.7665733997
 H,0,-2.8646426637,1.1744209611,2.7573291688
 H,0,-4.2104184632,0.3129539418,1.9999164203
 H,0,-2.8511591293,-0.5923046016,2.6829173799
 H,0,-6.2479199795,-4.3499114176,-2.8363373423
```

```
H,0,-5.4720200737,-4.1186481437,-4.4096369561
H,0,-4.7294544856,-5.186975138,-3.2061506435
H,0,-4.0091080053,-0.8992505562,-6.1582715114
H,0,-5.1859852728,-1.4958777617,-4.9881204153
H,0,-3.928313331,-0.3553103239,-4.474994067
```

allene+dedm_dich_TS1_B.log
allene+dedm_TSA__dich_1 opt
B3LYP/6-31G*
E(RB3LYP) = -1634.03875147

Zero-point correction= 0.321527 (Hartree/Particle)
Thermal correction to Energy= 0.343572
Thermal correction to Enthalpy= 0.344516
Thermal correction to Gibbs Free Energy= 0.268497
Sum of electronic and ZPE= -1633.717224
Sum of electronic and thermal Energies= -1633.695180
Sum of electronic and thermal Enthalpies= -1633.69423
Sum of electronic and thermal Free Energies= -1633.77

```
     E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 215.595 77.497 159.996
```

```
C,0,-3.2040217663,0.213006071,2.0701365261
Al,0,-2.0641907745,0.2803958394,0.4676726352
C,0,-2.486938121,2.0306284172,-0.5776857377
C,0,-1.7134607232,2.1959709931,-1.7553201661
C,0,-0.7026303653,1.6645660995,-2.4109028372
Cl,0,0.0923800892,0.2889660306,0.9503568119
Cl,0,-2.4257744159,-1.400617911,-0.9199451275
C,0,-2.7581025,3.5484870915,-3.2728204834
C,0,-1.8775079856,4.3747988332,-2.5796375416
C,0,-0.5388491642,4.7945227947,-3.1664197878
C,0,0.6032785867,5.0457326196,-2.1709928853
C,0,-4.2152326124,3.3925824621,-2.9024370953
C,0,-2.4806797482,2.9978403641,-4.6547027017
C,0,-2.3097142822,5.1567801666,-1.3562245864
C,0,-2.7219129126,6.5994605287,-1.7179014396
H,0,-0.7318191058,5.7229992519,-3.726100607
H,0,-1.4876953707,5.1896085848,-0.6342520361
H,0,-3.1442695475,4.6731620498,-0.8486191434
H,0,-0.2001245828,4.0830483719,-3.9204130946
H,0,-2.9986568273,3.6338617651,-5.3853911297
```

```
 H,0,-1.4310730914,2.9711382237,-4.9427712559
 H,0,-2.8942703096,1.9899309348,-4.7565093121
 H,0,-4.810740344,3.9957864451,-3.6004935409
 H,0,-4.4693117308,3.7155363929,-1.894504426
 H,0,-4.5367506382,2.3534186139,-3.0304745165
 H,0,-0.2821858847,2.0498953266,-3.3284442122
 H,0,-0.2473738469,0.7616719736,-2.0067036785
 H,0,-3.5608749806,1.9143557789,-0.7586663476
 H,0,-2.3211109647,2.8117400366,0.1728242003
 H,0,-3.0174316769,-0.6982584641,2.6528531545
 H,0,-3.0207148996,1.0681860626,2.7339972668
 H,0,-4.2707136773,0.2213745453,1.8098828988
 H,0,1.521822459,5.2685357701,-2.7231814768
 H,0,0.4043805476,5.8956424097,-1.5114422973
 H,0,0.7895522935,4.1646717925,-1.5479868587
 H,0,-3.0452802211,7.1269778006,-0.814906443
 H,0,-1.8919958184,7.1626133052,-2.1563391462
 H,0,-3.5521240863,6.6067736283,-2.4322095812
```

allene+ICH_dich_TS1_A.log
allene+ICH_TSA1_1_dich opt
B3LYP/6-31G*
E(RB3LYP) = -1672.15268279

```
Zero-point correction= 0.330438 (Hartree/Particle)
Thermal correction to Energy= 0.351604
Thermal correction to Enthalpy= 0.352548
Thermal correction to Gibbs Free Energy= 0.278643
Sum of electronic and ZPE= -1671.822245
Sum of electronic and thermal Energies= -1671.801079
Sum of electronic and thermal Enthalpies= -1671.800135
Sum of electronic and thermal Free Energies= -1671.874040
```

```
     E      CV       S
  KCal/Mol Cal/Mol-K Cal/Mol-K
Total 220.635 76.309 155.546
```

```
 C,0,-3.767655,-0.890942,2.06258
 Al,0,-2.866232,-0.366008,0.394098
 Cl,0,-3.768677,1.425642,-0.535104
 C,0,-0.878534,0.073219,0.819611
 C,0,-0.125898,0.505467,-0.303827
 C,0,-0.249056,0.797355,-1.582139
 Cl,0,-2.863399,-1.970695,-1.125883
```

```
C,0,1.84252,1.495779,0.342414
C,0,2.10506,2.669891,-0.57285
C,0,2.115202,0.176304,-0.000849
C,0,1.540885,1.93674,1.754318
H,0,3.001765,3.191182,-0.211415
H,0,2.28161,2.409315,-1.615456
H,0,1.279973,3.38751,-0.526966
H,0,2.462498,2.342158,2.192844
H,0,1.186637,1.143159,2.40998
H,0,0.804162,2.747047,1.75618
H,0,0.554346,1.132207,-2.222386
H,0,-1.232482,0.699043,-2.039227
H,0,-0.962189,0.825913,1.611594
H,0,-0.531604,-0.873679,1.248755
H,0,-4.822151,-1.138613,1.885238
H,0,-3.297272,-1.772582,2.517687
H,0,-3.742754,-0.084042,2.806894
C,0,2.735796,-0.238811,-1.320289
C,0,4.219193,-0.625429,-1.093155
H,0,2.199205,-1.114693,-1.705579
H,0,2.679654,0.536461,-2.085181
C,0,4.354641,-1.736138,-0.04513
H,0,4.650284,-0.940128,-2.05054
H,0,4.777166,0.263129,-0.768539
C,0,3.6438,-1.356624,1.259016
H,0,3.916481,-2.663084,-0.441089
H,0,5.413517,-1.944734,0.149502
C,0,2.168883,-0.954291,1.005265
H,0,3.661825,-2.191834,1.968544
H,0,4.16723,-0.518867,1.738968
H,0,1.638219,-1.822266,0.591493
H,0,1.691175,-0.703724,1.952412
```

allene+ICH_dich_TS1_B.log
allene+ICH_TSA__dich_3 opt
B3LYP/6-31G*
E(RB3LYP) = -1672.15137956

Zero-point correction= 0.330063 (Hartree/Particle)
Thermal correction to Energy= 0.351243
Thermal correction to Enthalpy= 0.352187
Thermal correction to Gibbs Free Energy= 0.278399
Sum of electronic and ZPE= -1671.821317
Sum of electronic and thermal Energies= -1671.800137

```
Sum of electronic and thermal Enthalpies= -1671.799193
Sum of electronic and thermal Free Energies= -1671.872981

      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 220.408 76.569 155.301

 C,0,2.006457843,-3.4507244854,0.722013796
 C,0,2.0568001558,-2.8547472019,-0.6877222177
 C,0,2.8180719439,-1.5174486619,-0.7135168195
 C,0,2.3728401683,-0.5043905744,0.3242952478
 C,0,2.1537677581,-1.1025281493,1.7005417808
 C,0,1.3955342955,-2.4438794454,1.7007496055
 C,0,2.4396504805,0.8655827965,0.1057107144
 C,0,2.3930175567,1.87812094,1.2266295754
 C,0,2.9474760527,1.480939493,-1.1809087907
 C,0,0.0990945297,0.0773823867,-1.4937004439
 C,0,0.2119118084,0.3791711035,-0.2182332617
 C,0,-0.5289234875,0.7172871303,0.9359927204
 Al,0,-2.5633882279,1.0188783145,0.5633498788
 Cl,0,-3.3460311602,-0.7847796937,-0.4399025258
 C,0,-3.4471052854,1.387587607,2.2812191746
 Cl,0,-2.7013227785,2.6935577412,-0.8673850228
 H,0,3.8779048803,-1.7174130823,-0.4826708385
 H,0,3.1582721769,-1.2662302063,2.1235211637
 H,0,4.0027120932,1.7534581994,-1.042644613
 H,0,2.895070959,0.8327215528,-2.0547609092
 H,0,2.4035783017,2.4039103869,-1.4035256144
 H,0,3.4260125543,2.1494033629,1.483598401
 H,0,1.9138826545,1.52608866,2.1386305917
 H,0,1.8949760751,2.7972173795,0.9004860531
 H,0,0.9211400801,-0.1782300603,-2.1466088489
 H,0,-0.8957866742,0.0886476625,-1.9371681355
 H,0,-0.2593409764,1.6805743654,1.3810496774
 H,0,-0.5409336163,-0.0613384061,1.7065948017
 H,0,-4.519296711,1.5777058599,2.143857921
 H,0,-3.3513626386,0.5417230016,2.9746225861
 H,0,-3.0190353253,2.2693048063,2.7759174035
 H,0,2.818056379,-1.1041242412,-1.7234458425
 H,0,1.661132825,-0.3997062646,2.3743608147
 H,0,1.393952103,-2.8437659401,2.7211958787
 H,0,0.3456291447,-2.2702834419,1.4293529944
 H,0,1.4236794424,-4.3793875597,0.721072193
 H,0,3.0229956736,-3.7137308642,1.0487783347
```

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 H,0,2.5412215255,-3.5469918775,-1.3859220861
 H,0,1.0340814201,-2.6973755935,-1.0539653382

allene+tme_dich_TS1.log
 allene+tme_TSA__dich opt
B3LYP/6-31G*
E(RB3LYP) = -1555.41608584

Zero-point correction= 0.263392 (Hartree/Particle)
Thermal correction to Energy= 0.283066
Thermal correction to Enthalpy= 0.284010
Thermal correction to Gibbs Free Energy= 0.213893
Sum of electronic and ZPE= -1555.152694
Sum of electronic and thermal Energies= -1555.133020
Sum of electronic and thermal Enthalpies= -1555.132076
Sum of electronic and thermal Free Energies= -1555.202193

     E     CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 177.627 68.087 147.574

 C,0,2.6303414387,-1.3238530746,1.598425984
 C,0,2.7969217981,-0.6475306301,0.2596681523
 C,0,2.73962075,0.7326848261,0.0968949099
 C,0,2.5088978838,1.6864835695,1.2433251163
 C,0,3.213481479,1.4459090048,-1.1481184942
 C,0,3.3440406762,-1.5885078514,-0.7886281876
 H,0,2.1174694519,-2.2845104851,1.4848651851
 H,0,2.1012511461,-0.7313380629,2.3426459329
 H,0,3.6300276373,-1.5400141268,1.9985283594
 H,0,4.354966394,-1.8884488123,-0.480835478
 H,0,2.7421412498,-2.5007769207,-0.8414321448
 H,0,3.4245511736,-1.1650961383,-1.7885132874
 H,0,4.1838726609,1.9096827501,-0.925264449
 H,0,3.3550782225,0.8070015976,-2.018513152
 H,0,2.5261418772,2.2544913053,-1.4148132128
 H,0,3.483486581,2.084031553,1.5568153081
 H,0,2.0430662907,1.2388078633,2.1192069896
 H,0,1.9054133274,2.5413227848,0.9206905434
 C,0,0.6651840468,-0.1004854794,-0.303400312
 C,0,0.5999362729,-0.2478832927,-1.6115751424
 H,0,1.4494194272,-0.288365525,-2.2776859318
 H,0,-0.3836351946,-0.3440956754,-2.0682851227
 C,0,-0.1786234337,-0.0251192244,0.8399850963
```

```
 H,0,-0.0818980427,0.9110807972,1.4011274527
 H,0,-0.0663622432,-0.8727952884,1.5253854628
 Al,0,-2.2119704209,-0.0308732008,0.4170058951
 Cl,0,-2.6548448371,-1.8070851935,-0.8242470368
 Cl,0,-2.6141486606,1.7553637386,-0.8228840507
 C,0,-3.212569876,-0.0271047714,2.111609775
 H,0,-4.2956188179,-0.0034410106,1.9348111003
 H,0,-2.9994937774,-0.9233913897,2.7091760489
 H,0,-2.9639964812,0.8460923636,2.7293186901
```

```
allene_dich_freq.log
 allene_dich opt
B3LYP/6-31G*
E(RB3LYP) = -116.659093199

Zero-point correction= 0.055389 (Hartree/Particle)
Thermal correction to Energy= 0.059146
Thermal correction to Enthalpy= 0.060091
Thermal correction to Gibbs Free Energy= 0.031298
Sum of electronic and ZPE= -116.603705
Sum of electronic and thermal Energies= -116.599947
Sum of electronic and thermal Enthalpies= -116.599003
Sum of electronic and thermal Free Energies= -116.627796

     E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 37.115 11.707 60.600

 C,0,0.5904477556,0.1272123888,0.3013119842
 C,0,0.0428114421,-0.1039716919,1.4658422077
 C,0,1.1391768559,0.3586047011,-0.8630609498
 H,0,0.5882982806,-0.6094135947,2.2609846424
 H,0,-0.9787816334,0.1995306315,1.6867521536
 H,0,1.0710437584,-0.360728173,-1.6770209834
 H,0,1.6862695407,1.2779307381,-1.0633920547
```

```
AlMeCl2_dich_freq.log
 AlMeCl2_dich opt
B3LYP/6-31G*
E(RB3LYP) = -1202.89939779

Zero-point correction= 0.038927 (Hartree/Particle)
Thermal correction to Energy= 0.045391
Thermal correction to Enthalpy= 0.046335
```

```
Thermal correction to Gibbs Free Energy= 0.006521
Sum of electronic and ZPE= -1202.860471
Sum of electronic and thermal Energies= -1202.854007
Sum of electronic and thermal Enthalpies= -1202.853063
Sum of electronic and thermal Free Energies= -1202.892877

     E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 28.483 19.061 83.796

 Al,0,0.9764767418,0.5520590638,-0.0771771821
 C,0,0.0970613928,0.0512995014,1.5750736606
 Cl,0,2.402449867,-0.676390318,-1.0634388441
 Cl,0,0.5912499187,2.3975909408,-1.058535616
 H,0,-0.9904478571,0.0389562516,1.4379460676
 H,0,0.417207748,-0.9390013983,1.913363201
 H,0,0.3243834922,0.7800264332,2.361778713

dedm_dich_freq.log
 dedm_dich opt
B3LYP/6-31G*
E(RB3LYP) = -314.482587647

Zero-point correction= 0.222285 (Hartree/Particle)
Thermal correction to Energy= 0.233300
Thermal correction to Enthalpy= 0.234244
Thermal correction to Gibbs Free Energy= 0.185882
Sum of electronic and ZPE= -314.260303
Sum of electronic and thermal Energies= -314.249288
Sum of electronic and thermal Enthalpies= -314.248343
Sum of electronic and thermal Free Energies= -314.296705

     E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 146.398 38.911 101.786

 C,0,-0.1947554888,0.2453079017,-0.020244395
 C,0,-0.0111621665,-0.1381106475,1.2607406572
 C,0,0.9464287692,0.6386034262,-0.9473760111
 C,0,1.3450614896,-0.2478427121,1.9242869902
 C,0,-1.1376189493,-0.5090749146,2.2015969941
 C,0,1.4710631608,-0.5362262721,-1.7935632306
 H,0,0.589844152,1.4256932795,-1.6259847158
 H,0,1.7805922034,1.080753331,-0.3932079835
```

```
 H,0,2.2432256366,-0.2011516767,-2.4964695114
 H,0,1.9065288553,-1.313745372,-1.155632736
 H,0,0.6661187477,-0.9985842068,-2.37721586
 H,0,-1.0445546892,-1.5542595376,2.5308132945
 H,0,-1.0876233385,0.1028250304,3.1134691408
 H,0,-2.1333933896,-0.3792754734,1.7739529515
 H,0,1.4215194181,0.4440049234,2.7757156069
 H,0,1.4842352932,-1.2565655136,2.3384019494
 H,0,2.1838638611,-0.0495493498,1.254643219
 C,0,-1.5636494129,0.32743039,-0.6807432501
 H,0,-1.4573224549,0.0548934069,-1.7399043097
 H,0,-2.2600399099,-0.4023194968,-0.2554187527
 C,0,-2.1920598886,1.730864065,-0.5975648682
 H,0,-3.1441174451,1.7689337786,-1.1404240803
 H,0,-2.3830720421,2.0124654083,0.4442062991
 H,0,-1.5303324117,2.4906102321,-1.0302513985
```

```
che_dich_freq.log
 ich_dich opt
B3LYP/6-31G*
E(RB3LYP) = -352.593835898

Zero-point correction= 0.231728 (Hartree/Particle)
Thermal correction to Energy= 0.241420
Thermal correction to Enthalpy= 0.242364
Thermal correction to Gibbs Free Energy= 0.197263
Sum of electronic and ZPE= -352.362108
Sum of electronic and thermal Energies= -352.352416
Sum of electronic and thermal Enthalpies= -352.351472
Sum of electronic and thermal Free Energies= -352.396573

     E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 151.493 37.426 94.923

 C,0,-2.0313656275,1.5303795292,0.0941687995
 C,0,-1.2774901348,0.3832322012,-0.5576349556
 C,0,-0.418492928,-0.3683935261,0.1479520562
 C,0,-0.0958140728,-0.1749980785,1.6102067782
 C,0,-0.603542216,1.1714291211,2.1469203883
 C,0,-2.0173149496,1.4571269761,1.6285343433
 C,0,-1.5214315904,0.110408446,-2.036163543
 H,0,-0.8075478008,-0.6677429774,-2.3400105762
 C,0,-2.9363423801,-0.4428757581,-2.302050812
```

H,0,0.0947758801,-1.1903568817,-0.3536639215
H,0,-0.5356923817,-1.0005873176,2.1932235414
H,0,0.9894779624,-0.259699779,1.762671739
H,0,-0.5812502854,1.1763325411,3.2435929249
H,0,0.0691825851,1.9738201915,1.8124888718
H,0,-2.6925116591,0.6558426667,1.9609264579
H,0,-2.4047421176,2.3926261662,2.050657376
H,0,-3.0685279295,1.5525913205,-0.2663076333
C,0,-1.2524993173,1.3502631433,-2.9110107812
H,0,-3.0549487728,-0.6975764307,-3.3622060431
H,0,-3.123839427,-1.3471931912,-1.712236277
H,0,-3.7125204361,0.2901677853,-2.0521586014
H,0,-1.5906616621,2.4858358742,-0.2303283613
H,0,-1.3620885438,1.1015176986,-3.9733025668
H,0,-1.9570147959,2.1603461862,-2.6878050594
H,0,-0.2375173994,1.7339500931,-2.7553241447

ich_dich_freq.log
ich_dich opt
B3LYP/6-31G*
E(RB3LYP) = -352.593333206

Zero-point correction= 0.231602 (Hartree/Particle)
Thermal correction to Energy= 0.241488
Thermal correction to Enthalpy= 0.242432
Thermal correction to Gibbs Free Energy= 0.196609
Sum of electronic and ZPE= -352.361731
Sum of electronic and thermal Energies= -352.351845
Sum of electronic and thermal Enthalpies= -352.350901
Sum of electronic and thermal Free Energies= -352.396725

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	151.536	37.587	96.443

C,0,0.8684385707,-1.5356028607,-0.5044310478
C,0,-0.2292266531,-0.7567061283,0.2014982896
C,0,-1.4792520197,-0.6897215418,-0.6603744911
C,0,-1.1813651191,-0.0712882494,-2.0434628203
C,0,-0.0562165875,-0.8239433574,-2.7665085714
C,0,1.196031453,-0.9275687503,-1.8854110612
C,0,-0.1003859366,-0.1756539517,1.4139051882
C,0,1.1542342489,-0.2311323338,2.26111298
C,0,-1.1924527176,0.6144879408,2.1052623218

```
H,0,-1.8520918593,-1.7149401465,-0.818583254
H,0,-2.2913991065,-0.138060176,-0.1821256199
H,0,-2.09437511,-0.0719980143,-2.6529786821
H,0,-0.8904474181,0.9801352004,-1.9082839806
H,0,-0.4045176344,-1.8372216176,-3.0170685569
H,0,0.184435057,-0.3312868705,-3.7174899305
H,0,1.9642025274,-1.5335179027,-2.3832420252
H,0,1.6257216422,0.0738513117,-1.7407496391
H,0,0.520131374,-2.569625223,-0.6612472865
H,0,1.7827725407,-1.6062308671,0.0885619746
H,0,-0.8502408493,1.6384340936,2.3131452523
H,0,-2.1236260691,0.6857115457,1.5414716519
H,0,-1.4283378514,0.168366341,3.0820844984
H,0,1.5190517033,0.7845732376,2.4709702416
H,0,0.9365626226,-0.6842767036,3.2389262605
H,0,1.9764071918,-0.7912299762,1.813509308
```

Part III

anisaldehydeM062XPS
anisaldehde for Wittig anisaldehyde and ketone
M062X/6-31+G**
E(RM062X) = -459.931869643

Zero-point correction= 0.143666 (Hartree/Particle)
Thermal correction to Energy= 0.152525
Thermal correction to Enthalpy= 0.153469
Thermal correction to Gibbs Free Energy= 0.109554
Sum of electronic and ZPE= -459.788204
Sum of electronic and thermal Energies= -459.779345
Sum of electronic and thermal Enthalpies= -459.778400
Sum of electronic and thermal Free Energies= -459.822315

```
      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 95.711 32.954 92.426
```

```
C,0,-0.0013640658,0.,0.116042051
C,0,0.0521638259,0.,1.5185415556
C,0,1.2897465865,0.,2.1501136661
C,0,2.4733095825,0.,1.4061254485
C,0,2.4059915729,0.,0.005585956
```

C,0,1.1814093891,0.,-0.6391548467
H,0,-0.8535870545,0.,2.1121104867
H,0,1.3488913963,0.,3.2346071802
C,0,3.7867627504,0.,2.0688875787
H,0,3.3235661101,0.,-0.5778027297
H,0,1.1080782896,0.,-1.7213649287
O,0,-1.1492158283,0.,-0.5951452003
C,0,-2.3821803926,0.,0.1139268221
H,0,-3.1615617058,0.,-0.6457521632
H,0,-2.4740699039,-0.8961228929,0.7358676169
H,0,-2.4740699039,0.8961228929,0.7358676169
O,0,3.9551191481,0.,3.2749419227
H,0,4.6586332033,0.,1.3859979675

anisaldehydeM062XpsSMD
anisaldehyde smd
M062X/6-31+G**
E(RM062X) = -459.938435544

Zero-point correction= 0.143526 (Hartree/Particle)
Thermal correction to Energy= 0.152469
Thermal correction to Enthalpy= 0.153413
Thermal correction to Gibbs Free Energy= 0.108920
Sum of electronic and ZPE= -459.794910
Sum of electronic and thermal Energies= -459.785967
Sum of electronic and thermal Enthalpies= -459.785023
Sum of electronic and thermal Free Energies= -459.829515

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 95.675 32.982 93.642

C,0,-0.001756808,0.,0.1136134217
C,0,0.0509603378,0.,1.5164371717
C,0,1.2877869036,0.,2.1500292541
C,0,2.4724693189,0.,1.4078683694
C,0,2.4064341114,0.,0.0072144345
C,0,1.1826928602,0.,-0.6396578988
H,0,-0.8560537351,0.,2.1087846241
H,0,1.3420322457,0.,3.2352686537
C,0,3.7879562513,0.,2.0683643152
H,0,3.326222681,0.,-0.5735442068
H,0,1.1136607353,0.,-1.7227395607
O,0,-1.1485706533,0.,-0.5963029145

```
 C,0,-2.3807105635,0.,0.1162059185
 H,0,-3.1631616202,0.,-0.6419336032
 H,0,-2.4741508758,-0.8968708553,0.7376804493
 H,0,-2.4741508758,0.8968708553,0.7376804493
 O,0,3.9592517123,0.,3.2734220908
 H,0,4.6567109739,0.,1.381005032
```

OP1directM062XPCMPS
OP1 direct for Wittig anisaldehyde and ketone for polyrate
M062X/6-31+G**
E(RM062X) = -1687.80686728

Zero-point correction= 0.489706 (Hartree/Particle)
Thermal correction to Energy= 0.518930
Thermal correction to Enthalpy= 0.519874
Thermal correction to Gibbs Free Energy= 0.427861
Sum of electronic and ZPE= -1687.317162
Sum of electronic and thermal Energies= -1687.287937
Sum of electronic and thermal Enthalpies= -1687.286993
Sum of electronic and thermal Free Energies= -1687.379006

```
      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 325.634 114.931 193.658
```

```
 O,0,0.9049070255,0.9001795991,1.1164902508
 C,0,1.7178983463,-0.2554776447,1.0235526006
 P,0,-0.5915921416,0.164736521,0.4052027081
 C,0,0.7922748475,-1.1140758489,0.1604534248
 C,0,3.0831436926,0.0251228952,0.4400668696
 C,0,-1.8678950998,-0.9630732779,-0.4769282395
 C,0,-1.9156784164,-0.9946306033,-1.8783114332
 C,0,-2.6422353125,-1.9727825942,-2.5591755785
 C,0,-3.3357296095,-2.9516651552,-1.8480556718
 C,0,-3.2902228156,-2.9452907154,-0.4547534279
 C,0,-2.5598177298,-1.9652830025,0.2191895155
 C,0,-0.789869983,1.6016338895,-0.73162622
 C,0,-1.5051718985,0.3484903116,1.9961674036
 C,0,0.3283180196,2.228537883,-1.2888501482
 C,0,0.1697559668,3.294356302,-2.1753169834
 C,0,-1.104333836,3.7641887125,-2.4857153341
 C,0,-2.2244212586,3.1498542798,-1.924453487
 C,0,-2.0675705059,2.0621344202,-1.0694381356
 C,0,-2.896284141,0.5172033304,2.0019571834
```

```
C,0,-3.5844936751,0.7126027939,3.1964604712
C,0,-2.8956923529,0.7053848139,4.4087566065
C,0,-1.5154207525,0.5180342163,4.4159621563
C,0,-0.8212746325,0.3579809425,3.21715216
C,0,3.9043278849,-1.0307027685,0.0206417222
C,0,5.1727154582,-0.7917766003,-0.485605722
C,0,5.6522482165,0.5219154939,-0.5812313556
C,0,4.8502413696,1.5842083681,-0.1631399042
C,0,3.5733977431,1.323052386,0.3460866367
H,0,1.8380034628,-0.7329947574,2.009594201
H,0,1.0583781238,-1.0991909469,-0.9042082979
H,0,-1.3761822441,-0.2488631967,-2.4582854886
H,0,-2.6635829982,-1.9696914237,-3.644989006
H,0,-3.9028806115,-3.7125797005,-2.3752175656
H,0,-3.8188509596,-3.7056617196,0.1122929101
H,0,-2.5268788415,-1.9953267238,1.3053013623
H,0,1.3225837575,1.8858367869,-1.0249482011
H,0,1.0456585305,3.7626876564,-2.6133229312
H,0,-1.2259965626,4.6034294588,-3.1635252996
H,0,-3.2212920561,3.5082748348,-2.1608587347
H,0,-2.9517283011,1.5697546618,-0.6782953151
H,0,-3.4598676628,0.4808480923,1.0761493319
H,0,-4.6599287174,0.8575567858,3.1778058431
H,0,-3.433380632,0.8428944432,5.3418773706
H,0,-0.9709169092,0.5066262094,5.3548841991
H,0,0.2556998403,0.2489404583,3.2324466769
H,0,3.5483198995,-2.0569351177,0.0932676261
H,0,5.8116997715,-1.6053529619,-0.8138512161
O,0,6.9067294144,0.6598514231,-1.0925408303
H,0,5.1977645487,2.6087628122,-0.2219127086
H,0,2.9460441467,2.1451359285,0.6774675342
C,0,0.4842989238,-2.5212168616,0.6293030003
C,0,0.2914231972,-3.5768405463,-0.425430959
O,0,0.4187022019,-2.7676251084,1.8202689549
H,0,-0.0613431785,-4.5036474229,0.027451833
H,0,-0.4162519321,-3.2294212335,-1.1857940564
H,0,1.2508549478,-3.7500811193,-0.9270539831
C,0,7.4318706154,1.9725318172,-1.2003238084
H,0,8.4307699208,1.8635934128,-1.6202533569
H,0,6.8186338329,2.5873366054,-1.8682711076
H,0,7.4973920615,2.4517255053,-0.2173720461
```

OP1M062XPS

OP1 for Wittig anisaldehyde and ketone

```
M062X/6-31+G**
E(RM062X) = -1687.80137367

Zero-point correction= 0.489413 (Hartree/Particle)
Thermal correction to Energy= 0.518151
Thermal correction to Enthalpy= 0.519095
Thermal correction to Gibbs Free Energy= 0.428637
Sum of electronic and ZPE= -1687.311961
Sum of electronic and thermal Energies= -1687.283223
Sum of electronic and thermal Enthalpies= -1687.282279
Sum of electronic and thermal Free Energies= -1687.372736

      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 325.145 113.159 190.384

 O,0,1.1154330473,0.9455978688,0.8327929512
 C,0,1.788113766,-0.2586053641,0.5855660241
 P,0,-0.5199423093,0.3322590741,0.1516847244
 C,0,0.8336838584,-0.7965213747,-0.5065919483
 C,0,3.2179124182,-0.0759058485,0.1428366949
 C,0,-1.9878251096,-0.5290780776,-0.6909467352
 C,0,-1.8216000439,-1.1352095821,-1.9421817608
 C,0,-2.8971741503,-1.6960339546,-2.6313565439
 C,0,-4.1751166784,-1.6552808428,-2.0767823305
 C,0,-4.3648002194,-1.0445212614,-0.8375557753
 C,0,-3.2824990252,-0.4856771086,-0.1575431098
 C,0,-0.8463102299,2.0201783878,-0.5537017312
 C,0,-1.1083073689,0.1321795257,1.8820947306
 C,0,-0.106446172,3.1266552151,-0.1000699587
 C,0,-0.3709946445,4.4075014513,-0.5788365362
 C,0,-1.3596546277,4.6115040291,-1.540350611
 C,0,-2.0869124217,3.5228643228,-2.0121814349
 C,0,-1.8407860129,2.2415524839,-1.5183357754
 C,0,-1.1445725465,1.2520805396,2.7190098801
 C,0,-1.5928974902,1.1319993533,4.0320336273
 C,0,-1.977392939,-0.1141105498,4.5285274791
 C,0,-1.9221305831,-1.2351694092,3.7026829484
 C,0,-1.5025103295,-1.1131675564,2.3772496997
 C,0,4.1753898014,-1.0642803479,0.3973825604
 C,0,5.4797849844,-0.9288971358,-0.0592580637
 C,0,5.8525021817,0.2131056585,-0.7778679967
 C,0,4.9096459592,1.2133920814,-1.0328853186
 C,0,3.6014471956,1.0570916019,-0.570482892
```

```
H,0,1.7603063995,-0.936972963,1.4565093249
H,0,1.1507636445,-0.3786425724,-1.4703501827
H,0,-0.8443850457,-1.1539796033,-2.4197869265
H,0,-2.7361476446,-2.1594473588,-3.6000676067
H,0,-5.0161931225,-2.0906778475,-2.6073889358
H,0,-5.3572094432,-0.9987934627,-0.3989886734
H,0,-3.4589680525,-0.0012173022,0.799192515
H,0,0.6864063663,2.9783569985,0.6209744811
H,0,0.2085049628,5.245626276,-0.2042003146
H,0,-1.5577107258,5.6091069224,-1.9203507752
H,0,-2.8562710346,3.6630465196,-2.7648884621
H,0,-2.4357105673,1.4229553209,-1.9022689972
H,0,-0.8221090201,2.2204532712,2.3483557417
H,0,-1.6319120061,2.0102888439,4.6688449046
H,0,-2.3159221487,-0.2095957576,5.55569571
H,0,-2.2131578375,-2.2089039825,4.0843505958
H,0,-1.4745665831,-1.9842786068,1.7310888894
H,0,3.8978341698,-1.9500719344,0.9654867912
H,0,6.22824134,-1.6897866022,0.1374362972
O,0,7.1522124116,0.2659363882,-1.1796917375
H,0,5.1781561863,2.1104705208,-1.5779185461
H,0,2.8639215616,1.8339633524,-0.7561091949
C,0,0.6946300893,-2.2987507633,-0.5816002159
C,0,1.4795174958,-2.9835195933,-1.6703947526
O,0,0.0496294549,-2.9191540797,0.2426525376
H,0,1.4098914671,-4.0661488774,-1.5666009985
H,0,1.0988520009,-2.6775520035,-2.6509275638
H,0,2.5265992333,-2.6618988171,-1.6195302418
C,0,7.5689240144,1.4026704854,-1.9177810865
H,0,8.6230092234,1.2457486785,-2.1421492228
H,0,7.0052018055,1.4930454659,-2.8528314904
H,0,7.4524530944,2.3191979044,-1.3291936615
```

OP2M062XPCMPS
OP2 for Wittig anisaldehyde and ketone
M062X/6-31+G**
E(RM062X) = -1687.80648383

Zero-point correction= 0.489648 (Hartree/Particle)
Thermal correction to Energy= 0.519299
Thermal correction to Enthalpy= 0.520244
Thermal correction to Gibbs Free Energy= 0.426953
Sum of electronic and ZPE= -1687.316835
Sum of electronic and thermal Energies= -1687.287184

Sum of electronic and thermal Enthalpies= -1687.286240
Sum of electronic and thermal Free Energies= -1687.379531

```
      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 325.865 115.155 196.347
```

```
O,0,-0.7376685808,-0.3603830814,-1.3304465244
C,0,-1.6634593024,0.7366469772,-1.0500164203
C,0,-1.0209979797,1.3665660111,0.1537873434
P,0,0.4345610235,-0.258265838,-0.186488885
H,0,-1.6330166786,1.410281034,-1.9113367815
H,0,-1.5460878404,1.2004271038,1.0944789303
C,0,2.612635411,-4.1265707039,-1.7005597735
C,0,1.3286989733,-3.8481127496,-2.1616942802
C,0,0.6612794023,-2.6954689352,-1.7386622542
C,0,1.2720507799,-1.8025574109,-0.8513996314
C,0,2.5640931079,-2.0969370138,-0.3943627764
C,0,3.2307444771,-3.2456540211,-0.8110676273
H,0,3.1307110699,-5.0217468396,-2.0306247267
H,0,0.8395226883,-4.5268914554,-2.8538821567
H,0,-0.3400478727,-2.4926592103,-2.1006447056
H,0,3.0614669421,-1.4242131126,0.3012991916
H,0,4.2313728696,-3.4522619554,-0.4439885429
C,0,3.8572242708,2.6743747534,-1.1486675847
C,0,3.7255655475,2.2103874786,0.1594407699
C,0,2.7005330553,1.324493657,0.4913998528
C,0,1.8050439387,0.8995484314,-0.4940788976
C,0,1.9396077387,1.3618756148,-1.8067728947
C,0,2.9641923811,2.2471311831,-2.1310171349
H,0,4.6546789989,3.3655341937,-1.4025144573
H,0,4.4237836824,2.5320331029,0.9257894505
H,0,2.6184779767,0.9607605698,1.5115133675
H,0,1.2392600995,1.0354888563,-2.5716922154
H,0,3.0610710376,2.6062773214,-3.1505801391
C,0,0.0535548874,-1.6613688806,4.2209770581
C,0,-0.0326436949,-2.585106849,3.1827211979
C,0,0.1080001182,-2.1678723288,1.8583898068
C,0,0.2954308715,-0.8129723214,1.563401061
C,0,0.347039654,0.1132179289,2.6118288919
C,0,0.2537381306,-0.3097211439,3.9333735914
H,0,-0.0415547436,-1.9895227537,5.2512235148
H,0,-0.1983147897,-3.6358879711,3.3976366595
H,0,0.069762517,-2.9022965724,1.0595434927
```

```
H,0,0.4567384447,1.1716518713,2.3963024312
H,0,0.3189858287,0.4166763525,4.7371449427
C,0,-5.6612315919,-0.7561441073,-0.4254849263
C,0,-5.4431964818,0.3162084772,-1.2908559647
C,0,-4.1379027778,0.77363469,-1.4975282419
C,0,-3.0519866507,0.1912356954,-0.8527168381
C,0,-3.2901303651,-0.8851364406,0.0144513927
C,0,-4.5750854414,-1.3575169364,0.2265636715
O,0,-6.8837124482,-1.2884508926,-0.1544993977
H,0,-6.2630099535,0.7960211814,-1.8116640505
H,0,-3.9731906999,1.6049513434,-2.1785303859
H,0,-2.4580792774,-1.3628534378,0.5282282669
H,0,-4.7659161233,-2.1921807972,0.8935456436
C,0,-0.5319640614,2.738919665,-0.0048223081
C,0,-0.1419164853,3.5051166812,1.2445315382
O,0,-0.3629559797,3.2648404245,-1.106235111
H,0,-0.2992992043,4.5722935415,1.0772652986
H,0,-0.6971199391,3.1799468976,2.1275694449
H,0,0.9291223507,3.3508800777,1.4259453049
C,0,-8.0097625682,-0.710406347,-0.7943247174
H,0,-8.8744664069,-1.2762859832,-0.4510516209
H,0,-8.1245957692,0.3420668643,-0.5124880566
H,0,-7.9274665668,-0.7917678904,-1.8836930863
```

Ph3PCHCOMeM062XPS
Ph3PCHCOMe for Wittig anisaldehyde and ketone
M062X/6-31+G**
E(RM062X) = -1227.87396966

Zero-point correction= 0.340415 (Hartree/Particle)
Thermal correction to Energy= 0.361450
Thermal correction to Enthalpy= 0.362394
Thermal correction to Gibbs Free Energy= 0.286508
Sum of electronic and ZPE= -1227.533555
Sum of electronic and thermal Energies= -1227.512520
Sum of electronic and thermal Enthalpies= -1227.511575
Sum of electronic and thermal Free Energies= -1227.587462

```
      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 226.813 80.224 159.716
```

```
C,0,0.3940928673,0.1446599875,0.4188664096
P,0,0.4339366656,-0.1266168487,2.1266935761
```

```
H,0,-0.2933816759,0.8962840058,0.0524987633
C,0,4.3209634101,1.1083726773,4.2798873919
C,0,3.0982574515,1.2474618773,4.9357072645
C,0,1.9168889283,0.881983157,4.2918393398
C,0,1.9611626191,0.3719833541,2.9891110439
C,0,3.1886107044,0.2341704322,2.3299958872
C,0,4.3647275152,0.6032889851,2.9799871088
H,0,5.2400498754,1.3966598587,4.7805842261
H,0,3.061266192,1.6434271496,5.9454451586
H,0,0.9649179896,1.0021666597,4.8027335484
H,0,3.212592375,-0.1730443145,1.3231247497
H,0,5.3166191513,0.4976547868,2.4694630823
C,0,-0.5229530696,-4.4704397964,3.3197781208
C,0,0.2538551091,-3.6835960621,4.1691522943
C,0,0.5768166451,-2.3758423464,3.8087761795
C,0,0.1145743566,-1.8549901734,2.5969121145
C,0,-0.6565947079,-2.6468001817,1.7416470153
C,0,-0.9752314326,-3.9529745337,2.1053647276
H,0,-0.7697344684,-5.4898165249,3.5995567255
H,0,0.6146427239,-4.0870355384,5.1097702805
H,0,1.1915908529,-1.7711021023,4.469565276
H,0,-0.9936645091,-2.2390824083,0.7923567174
H,0,-1.5690880379,-4.5687120048,1.4374704024
C,0,-2.8974752437,2.5014769649,3.9162148428
C,0,-1.8223503529,3.0784794996,3.2369259797
C,0,-0.8181650764,2.2716147652,2.7115309582
C,0,-0.8866473124,0.8803998525,2.8636521437
C,0,-1.9603558225,0.3043840895,3.5465651615
C,0,-2.9652843406,1.1187727939,4.0705597018
H,0,-3.6806216933,3.132036329,4.3253098612
H,0,-1.7655029552,4.1556907964,3.1186750423
H,0,0.0221752657,2.7221986823,2.1888856533
H,0,-2.0181249474,-0.7731894875,3.6700823758
H,0,-3.7999479871,0.6691344774,4.5985494579
C,0,1.1609582006,-0.676605509,-0.4298121722
C,0,1.0094029358,-0.4957353294,-1.9306134624
O,0,1.9510634438,-1.5591988986,-0.0128435181
H,0,1.9926762028,-0.2980087672,-2.3667353211
H,0,0.6407655357,-1.4315128141,-2.3617760348
H,0,0.3265796161,0.3141814597,-2.1947210736
```

product for Wittig anisaldehyde and ketone
M062X/6-31G*
E(RM062X) = -576.574595639

```
Zero-point correction= 0.206518 (Hartree/Particle)
Thermal correction to Energy= 0.219345
Thermal correction to Enthalpy= 0.220289
Thermal correction to Gibbs Free Energy= 0.165203
Sum of electronic and ZPE= -576.368077
Sum of electronic and thermal Energies= -576.355251
Sum of electronic and thermal Enthalpies= -576.354307
Sum of electronic and thermal Free Energies= -576.409393

      E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 137.641 46.467 115.939

 C,0,0.1824181965,-0.4687530511,0.
 C,0,-0.4431313838,0.7815643809,0.
 C,0,-1.8290785745,0.9121391509,0.
 C,0,-2.6208048179,-0.238365995,0.
 C,0,-2.0117161916,-1.5036983384,0.
 C,0,-0.6359746033,-1.6137773505,0.
 H,0,0.1700289668,1.67901438,0.
 H,0,-2.2725536916,1.9005079367,0.
 O,0,-3.9728776474,-0.2392285437,0.
 H,0,-2.6482454065,-2.382341807,0.
 H,0,-0.1881047948,-2.6028383949,0.
 C,0,2.4172214778,-1.6281076301,0.
 C,0,1.6419448907,-0.531552777,0.
 H,0,2.1614474185,0.4270726426,0.
 H,0,2.00539227,-2.6340312302,0.
 C,0,3.8949456582,-1.4974344891,0.
 C,0,4.6765070465,-2.7907783409,0.
 O,0,4.4533688463,-0.4127762191,0.
 H,0,5.746682365,-2.5828607887,0.
 H,0,4.4131040499,-3.3859171329,0.8810694519
 H,0,4.4131040499,-3.3859171329,-0.8810694519
 C,0,-4.6338208166,1.0142687123,0.
 H,0,-5.7003161224,0.7921904348,0.
 H,0,-4.3797310883,1.5932007921,0.8946587821
 H,0,-4.3797310883,1.5932007921,-0.8946587821

TS1.5M062XpsSMD
 TS1.5 checking smd single point energy
M062X/6-31+G**
E(RM062X) = -1687.81472058
```

```
Zero-point correction= 0.487373 (Hartree/Particle)
Thermal correction to Energy= 0.516725
Thermal correction to Enthalpy= 0.517669
Thermal correction to Gibbs Free Energy= 0.425412
Sum of electronic and ZPE= -1687.327348
Sum of electronic and thermal Energies= -1687.297996
Sum of electronic and thermal Enthalpies= -1687.297052
Sum of electronic and thermal Free Energies= -1687.389309

      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 324.250 114.107 194.171

 O,0,0.7629964614,0.9877834096,1.3838372451
 C,0,1.2630900498,-0.1473385333,0.8687097306
 P,0,-1.2426942986,0.1050297503,0.0208473107
 C,0,0.4561405141,-0.3731921909,-0.4895077843
 C,0,2.7592864753,-0.1468963575,0.5673800386
 C,0,-2.3552937844,-0.7966146073,-1.1194280371
 C,0,-2.1110005846,-0.6819915745,-2.4951666443
 C,0,-2.9369056065,-1.3265842145,-3.4106274971
 C,0,-4.0177633855,-2.0872253765,-2.9594762096
 C,0,-4.2694318441,-2.1953108731,-1.5942885272
 C,0,-3.4414857294,-1.5509636037,-0.6726783436
 C,0,-1.6663114696,1.8486053134,-0.3016689813
 C,0,-1.7245793088,-0.3901831147,1.6924619571
 C,0,-0.7345763323,2.8796075199,-0.1368142735
 C,0,-1.1119029341,4.1959080698,-0.4004806882
 C,0,-2.4132195049,4.4916741168,-0.8036020565
 C,0,-3.345950908,3.4654498403,-0.9516010461
 C,0,-2.9745453693,2.1446058473,-0.711566109
 C,0,-2.3224550954,0.5457422396,2.5410103277
 C,0,-2.7402347374,0.1559753816,3.8103993192
 C,0,-2.5542758331,-1.1600358088,4.2364207531
 C,0,-1.9539863829,-2.0897235168,3.3886498837
 C,0,-1.542920509,-1.712939495,2.1104059605
 C,0,3.4928685422,-1.3382746463,0.4933734877
 C,0,4.8471207928,-1.3310376774,0.1844143123
 C,0,5.5031760755,-0.1157462516,-0.0523640813
 C,0,4.7904884253,1.0836065351,0.0271562227
 C,0,3.4272850803,1.0521371894,0.3378847464
 H,0,1.0624645233,-1.0643594926,1.4722616369
 H,0,0.7886818357,0.4058274981,-1.1864639851
```

H,0,-1.2795731071,-0.0798006193,-2.8577929665
H,0,-2.7384856024,-1.234260745,-4.474054162
H,0,-4.6615533079,-2.5928724429,-3.6728797783
H,0,-5.1111259563,-2.7815726404,-1.2381437158
H,0,-3.6516817444,-1.641587013,0.3886538045
H,0,0.2561276789,2.6262780993,0.2305922257
H,0,-0.3852878398,4.993603408,-0.2772312621
H,0,-2.702591575,5.5201207906,-0.9990234086
H,0,-4.3630320939,3.6882518982,-1.2591508696
H,0,-3.7079692363,1.3541769225,-0.8440237969
H,0,-2.4497186024,1.5757859804,2.2209364316
H,0,-3.2042833079,0.8836375729,4.4690476924
H,0,-2.8753457305,-1.45946665,5.2297166954
H,0,-1.8066980999,-3.1138135415,3.7177799775
H,0,-1.0876036163,-2.4390957265,1.4420048544
H,0,2.9964587784,-2.2887644227,0.6863036937
H,0,5.4186667792,-2.2531387798,0.131599087
O,0,6.8311684507,-0.2008314249,-0.3410985556
H,0,5.2800614712,2.0369803071,-0.136711712
H,0,2.8647830976,1.9783323409,0.423182352
C,0,0.5898720521,-1.7519396772,-1.0898575476
C,0,1.4719058639,-1.8816451401,-2.3000454232
O,0,0.0422682341,-2.7123198926,-0.5749342811
H,0,1.6992271241,-2.9304594911,-2.4962160506
H,0,0.9382428994,-1.4569194097,-3.1598745046
H,0,2.394240532,-1.3056599988,-2.1739456139
C,0,7.5322490027,1.0109360082,-0.5670669349
H,0,8.5671886504,0.7298038229,-0.7633014631
H,0,7.1320656041,1.5459613811,-1.4363329277
H,0,7.4940094433,1.6624947065,0.3136234915

TS1M062XPCMPS2
TS1 for Wittig anisaldehyde and ketone
M062X/6-31+G**
E(RM062X) = -1687.79361546

Zero-point correction= 0.485845 (Hartree/Particle)
Thermal correction to Energy= 0.515944
Thermal correction to Enthalpy= 0.516889
Thermal correction to Gibbs Free Energy= 0.422372
Sum of electronic and ZPE= -1687.307770
Sum of electronic and thermal Energies= -1687.277671
Sum of electronic and thermal Enthalpies= -1687.276727
Sum of electronic and thermal Free Energies= -1687.371243

```
     E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 323.760 115.482 198.926

 O,0,1.0622354854,1.3611509586,1.6251018877
 C,0,1.3708468669,0.2022348135,1.1777730313
 P,0,-1.3199308016,0.1405142383,-0.0248527823
 C,0,0.4113698257,-0.1107193547,-0.4193206255
 C,0,2.7947894799,-0.0437995595,0.7249337668
 C,0,-2.3783545629,-0.9027575369,-1.0702514072
 C,0,-2.1112610337,-0.9319325718,-2.4446660889
 C,0,-2.9229093281,-1.6749094355,-3.2946639943
 C,0,-4.0039430357,-2.3910913928,-2.7762862086
 C,0,-4.2733583896,-2.3583206958,-1.4103619719
 C,0,-3.4634786533,-1.6122913524,-0.5526997783
 C,0,-1.7689113052,1.8554070142,-0.4065223837
 C,0,-1.753635321,-0.2075442881,1.69867522
 C,0,-0.8692366907,2.8864459614,-0.1077103703
 C,0,-1.2295618327,4.2050364911,-0.3795121718
 C,0,-2.4728085557,4.4953025193,-0.9406500672
 C,0,-3.3679605741,3.4658660198,-1.2313351853
 C,0,-3.0196279122,2.1430543983,-0.9663571341
 C,0,-2.3621511573,0.7736963395,2.4855317924
 C,0,-2.7217858551,0.4779359159,3.7991347918
 C,0,-2.4744774748,-0.7897514221,4.3226189871
 C,0,-1.8667440253,-1.7683664043,3.5346349175
 C,0,-1.5043282534,-1.4832359413,2.2207650346
 C,0,3.3923816959,-1.298380824,0.8862841429
 C,0,4.6849439625,-1.5364025153,0.4372700265
 C,0,5.4062316762,-0.512455357,-0.1876518175
 C,0,4.8280847612,0.7519449683,-0.3443033896
 C,0,3.5297670063,0.9717193865,0.1198725106
 H,0,0.9848898885,-0.6910910705,1.7145067901
 H,0,0.7703322639,0.6969612702,-1.0599404531
 H,0,-1.2724074069,-0.3712796911,-2.8515256242
 H,0,-2.7121490962,-1.6972083152,-4.3588662315
 H,0,-4.6346400111,-2.9741459667,-3.4399050807
 H,0,-5.1130676139,-2.9144492672,-1.0065056852
 H,0,-3.6798284773,-1.5906737459,0.5110823825
 H,0,0.0836732597,2.6461699561,0.36310802
 H,0,-0.5363162666,5.0069999573,-0.1469512056
 H,0,-2.7451941413,5.5247526774,-1.1518379733
 H,0,-4.3360557872,3.6892464819,-1.6676752644
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 H,0,-3.7182439877,1.3449078554,-1.1999163212
 H,0,-2.5466060766,1.7652471915,2.083183107
 H,0,-3.1914914638,1.2404938339,4.4116613402
 H,0,-2.753864858,-1.0163057212,5.3468291228
 H,0,-1.6728145722,-2.7549761744,3.9429718064
 H,0,-1.0299210616,-2.237443432,1.5977573488
 H,0,2.8338032025,-2.100888394,1.3642074227
 H,0,5.1565980664,-2.5061482926,0.5616278685
 O,0,6.6626441034,-0.8362733834,-0.6030264932
 H,0,5.3721126971,1.5622692176,-0.8152509389
 H,0,3.0729547844,1.9522017326,0.0098227972
 C,0,0.7333009563,-1.4674937563,-0.8816159144
 C,0,1.7694898046,-1.6142989036,-1.9700980369
 O,0,0.2047985577,-2.4550089225,-0.3708100582
 H,0,2.2100016141,-2.6116414794,-1.930486855
 H,0,1.2670488391,-1.4864971297,-2.9368766013
 H,0,2.5485071756,-0.8513894002,-1.890490465
 C,0,7.4256383035,0.1723261422,-1.2439269903
 H,0,8.3789625377,-0.287605085,-1.5002316308
 H,0,6.930082322,0.5194926031,-2.1574947772
 H,0,7.5972644459,1.0221228381,-0.5741201385
```

```
TS2M062XPCMPS
 TS2 for Wittig anisaldehyde and ketone
M062X/6-31+G**
E(RM062X) = -1687.80610634

Zero-point correction= 0.488880 (Hartree/Particle)
Thermal correction to Energy= 0.517944
Thermal correction to Enthalpy= 0.518888
Thermal correction to Gibbs Free Energy= 0.426984
Sum of electronic and ZPE= -1687.317226
Sum of electronic and thermal Energies= -1687.288163
Sum of electronic and thermal Enthalpies= -1687.287218
Sum of electronic and thermal Free Energies= -1687.379122

      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 325.015 113.629 193.428

 O,0,0.2357799994,0.0691487315,-1.1787336888
 C,0,1.0752610493,-1.1134788204,-0.8511933405
 C,0,0.4392091209,-1.7164842201,0.3504041153
 P,0,-0.9893150036,0.1980474583,-0.1337076663
```

```
H,0,0.9818150929,-1.780454747,-1.7130294186
H,0,0.9067316134,-1.5124979189,1.3105272798
C,0,-2.8320476536,4.0790299752,-1.9152411082
C,0,-1.6670806722,3.5648874819,-2.4783237331
C,0,-1.0881057582,2.402102063,-1.9635558322
C,0,-1.6768325112,1.7445052157,-0.8799589555
C,0,-2.8512974301,2.2674612249,-0.3220577385
C,0,-3.4255738452,3.4267569755,-0.8325311986
H,0,-3.2786004739,4.9835472735,-2.3162751291
H,0,-1.2011145041,4.0678174943,-3.3199535783
H,0,-0.1789263754,2.0089419519,-2.4036033952
H,0,-3.3225308675,1.7715193647,0.5239885828
H,0,-4.3340311693,3.8203157255,-0.3878110131
C,0,-4.5736192787,-2.5681407434,-0.9043462772
C,0,-4.4616972507,-1.9460951436,0.3393642107
C,0,-3.3747970383,-1.1192137223,0.616234319
C,0,-2.3913224476,-0.9196829198,-0.3597246669
C,0,-2.503588747,-1.5411579279,-1.6072533139
C,0,-3.5952680785,-2.363097809,-1.8756792346
H,0,-5.4218123552,-3.2116906481,-1.1150682156
H,0,-5.2237861303,-2.0985308778,1.0969224707
H,0,-3.3099705379,-0.6281439672,1.5825197157
H,0,-1.7379181204,-1.3894819146,-2.3631167686
H,0,-3.6746923951,-2.8486011527,-2.8428843083
C,0,-0.2944845304,1.6756602867,4.184511546
C,0,-0.071106311,2.521809556,3.1013561197
C,0,-0.3051196179,2.0714176148,1.8019362629
C,0,-0.7275519446,0.7555884956,1.5828336539
C,0,-0.9216956682,-0.0999939891,2.6730554882
C,0,-0.7285256429,0.3654155496,3.9689300611
H,0,-0.1264009188,2.0321115449,5.195790153
H,0,0.2761476448,3.5371941074,3.2618582107
H,0,-0.1515873113,2.7457477399,0.9641188034
H,0,-1.209652613,-1.1334955725,2.5049196879
H,0,-0.900613335,-0.2986861889,4.809731406
C,0,5.1687734148,0.1476785132,-0.348901983
C,0,4.8462031838,-0.8088058306,-1.3112410733
C,0,3.5106180078,-1.1909953176,-1.4746082711
C,0,2.4972230079,-0.648629884,-0.6916112713
C,0,2.8410332157,0.3108569,0.2725214794
C,0,4.1563218631,0.7095528214,0.4431074782
O,0,6.4294456967,0.5987869758,-0.1062792653
H,0,5.6082652637,-1.2573701769,-1.937008322
H,0,3.2652877516,-1.9335671423,-2.2297130639
```

```
H,0,2.0667617894,0.7516772754,0.8976086816
H,0,4.428206168,1.4541876806,1.1846449997
C,0,-0.2102760063,-2.986887976,0.2136221431
C,0,-0.7410400089,-3.6482936027,1.4742392999
O,0,-0.437834243,-3.5353982173,-0.8797939359
H,0,-1.8184720969,-3.4482376233,1.5378252454
H,0,-0.6089440272,-4.7303810913,1.4025195614
H,0,-0.2599523366,-3.2785835949,2.3833221347
C,0,7.4806601063,0.0705432924,-0.8982924703
H,0,8.3906389307,0.5628404014,-0.5584641001
H,0,7.574490574,-1.0116691448,-0.7563038999
H,0,7.3197397619,0.2888831934,-1.9596728731
```

Part IV

```
MacB_Reactant_D2.out
E(RB3LYP) = -1311.19201937

Zero-point correction= 0.544170 (Hartree/Particle)
Thermal correction to Energy= 0.575015
Thermal correction to Enthalpy= 0.575959
Thermal correction to Gibbs Free Energy= 0.481296
Sum of electronic and ZPE= -1310.647849
Sum of electronic and thermal Energies= -1310.617005
Sum of electronic and thermal Enthalpies= -1310.616061
Sum of electronic and thermal Free Energies= -1310.710724

      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 360.827 116.937 199.235
```

```
MacB_Reactant_D2.out
E(RB3LYP) = -1311.19201937

Zero-point correction= 0.544170 (Hartree/Particle)
Thermal correction to Energy= 0.575015
Thermal correction to Enthalpy= 0.575959
Thermal correction to Gibbs Free Energy= 0.481296
```

Sum of electronic and ZPE= -1310.647849
Sum of electronic and thermal Energies= -1310.617005
Sum of electronic and thermal Enthalpies= -1310.616061
Sum of electronic and thermal Free Energies= -1310.710724

```
      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 360.827 116.937 199.235
```

C,0,-0.9903011624,-2.2095087861,0.8681387274
C,0,-1.9458196999,-2.0553557992,-0.0806261006
C,0,-3.3575514528,-2.2646734672,0.128708194
C,0,-4.2883711932,-1.9388114438,-0.7868374244
C,0,-4.6026998615,1.1461366812,-0.1226813112
C,0,-3.346912621,1.0214887559,0.3440199389
C,0,-5.8021003585,0.4175957563,0.4080317476
C,0,-5.7635737282,-1.9772142654,-0.5508790446
C,0,-6.4312921389,-0.5820965361,-0.5985291365
O,0,-7.8330332813,-0.7158663377,-0.3899194699
C,0,-2.2199635258,1.7459566039,-0.1940834068
C,0,0.1606776705,2.391523008,-0.3364776421
O,0,-0.0250047383,3.1930833933,-1.2547627309
C,0,-0.9435649424,1.5818502477,0.2184094576
C,0,2.800317342,-1.7133616049,1.2822143628
O,0,3.6641176238,-1.7810201524,2.1374610264
O,0,3.0243297112,-1.3696252562,-0.0115567814
C,0,1.377782361,-1.9983162781,1.5448645746
C,0,0.3977231448,-1.917034338,0.6178272133
C,0,4.3884323663,-1.1208419282,-0.4574868779
C,0,1.5298292848,2.1934730126,0.3100414828
C,0,2.6441980752,2.8967126692,-0.4983231168
C,0,4.0376301212,2.718071556,0.1121386549
C,0,4.474619731,0.3606332394,-0.8075363601
C,0,4.4120221911,1.2663383891,0.4308815442
C,0,4.6472334594,-2.0433597172,-1.6445521264
C,0,4.5153466827,-3.5255884077,-1.282238845
O,0,2.4169374972,4.298671539,-0.5788068567
C,0,1.4881465511,2.682038312,1.7720473363
H,0,-3.6716977631,-2.6376648527,1.1045564765
H,0,-1.6464420078,-1.6936106139,-1.064820183
H,0,-1.2685648325,-2.55098302,1.865486334
H,0,-3.957007533,-1.5467907286,-1.7489303958
H,0,-4.7851837367,1.8234233111,-0.9587853761
H,0,-3.145730759,0.3253481377,1.155938402

```
H,0,-5.5442833531,-0.1096887875,1.3374430118
H,0,-6.5886911429,1.1487684276,0.6406970814
H,0,-6.2715349949,-2.5990290366,-1.3010331507
H,0,-5.9695132566,-2.4153315288,0.4374766437
H,0,-6.339445987,-0.1720831981,-1.6111169124
H,0,-7.9569425854,-1.0842229885,0.5000132281
H,0,-2.4087918558,2.4788123173,-0.9786165907
H,0,-0.7003121176,0.8542452094,0.989302102
H,0,1.1645653396,-2.2974344907,2.5675709864
H,0,0.6607694924,-1.6062673081,-0.3914308756
H,0,5.0629853606,-1.3659872045,0.3686606014
H,0,2.6295512764,2.4642583578,-1.511403712
H,0,4.7629598876,3.1584798355,-0.5841653311
H,0,4.0786447478,3.3181876618,1.0289439772
H,0,5.4058708766,0.5458258066,-1.3594801149
H,0,3.649397003,0.5829989929,-1.4956043637
H,0,5.3845932987,1.2425016771,0.9386900111
H,0,3.6921298115,0.8533893753,1.1468579049
H,0,5.6594437533,-1.8306929077,-2.0138349603
H,0,3.9492095989,-1.7834944426,-2.4522800657
H,0,4.7368201384,-4.1642281416,-2.1453132004
H,0,5.2067809292,-3.7903413449,-0.4720404404
H,0,3.4972762697,-3.7470458896,-0.9426188947
H,0,1.5664125463,4.3781650316,-1.0486621053
H,0,1.7190815599,1.1095975381,0.3098527352
H,0,0.6251456837,2.2769749529,2.3121215484
H,0,1.435467831,3.7755375896,1.7826504416
H,0,2.3972564121,2.3719554168,2.2980331577
```

```
MacB_TS_Endo1_D2.out
E(RB3LYP) = -1311.15194796

Zero-point correction= 0.543301 (Hartree/Particle)
Thermal correction to Energy= 0.573070
Thermal correction to Enthalpy= 0.574014
Thermal correction to Gibbs Free Energy= 0.483226
Sum of electronic and ZPE= -1310.608647
Sum of electronic and thermal Energies= -1310.578878
Sum of electronic and thermal Enthalpies= -1310.577933
Sum of electronic and thermal Free Energies= -1310.668722

    E     CV       S
  KCal/Mol Cal/Mol-K Cal/Mol-K
Total 359.607 114.796 191.081
```

```
C,0,-1.6760602195,-1.796703244,-0.240994678
C,0,-2.3352777294,-1.9015923897,-1.458381792
C,0,-3.688373046,-1.6043307761,-1.6396957926
C,0,-4.4974714135,-1.1208178985,-0.5947223867
C,0,-3.9632142568,0.7369582956,-0.2603465142
C,0,-2.7066677417,0.8326894084,0.375547605
H,0,-4.0748496694,-1.5559995845,-2.6567487319
H,0,-1.7322357858,-2.1201699312,-2.3387040845
H,0,-2.2427741791,-1.6707484976,0.6754262872
H,0,-4.2781883138,-1.4905373661,0.4045603642
H,0,-3.9603853169,1.0820036041,-1.2944178889
H,0,-2.6708689004,0.6898305699,1.4563811311
C,0,-5.2296177178,1.1468028126,0.5058344347
H,0,-4.996362213,1.2846704319,1.5690434568
H,0,-5.5611027253,2.1194843569,0.1214054132
C,0,-5.9700195324,-0.8291520657,-0.7808099201
H,0,-6.1410766898,-0.332288561,-1.744513172
H,0,-6.5760595692,-1.7423860408,-0.7485457094
C,0,-6.3626850529,0.0957813044,0.3696615559
H,0,-7.3343508163,0.5780883857,0.1886328818
O,0,-6.4412094348,-0.7374716304,1.5298844619
H,0,-6.613953902,-0.1626932208,2.2911057691
C,0,-1.5258211967,1.2595922925,-0.2754026948
H,0,-1.5654188071,1.3956035347,-1.3559973918
C,0,0.7422111404,2.2153666681,-0.423424765
O,0,0.7329143463,2.2815432782,-1.653825959
C,0,-0.3538164445,1.6014735366,0.3419613439
H,0,-0.2556276856,1.5403564914,1.4233849248
C,0,1.8574493189,-1.6323273966,1.2078797444
O,0,2.4165779841,-1.2941750113,2.2362357705
O,0,2.4950538941,-2.0807017846,0.0959490932
C,0,0.3967693096,-1.586773217,1.0347107855
H,0,-0.1498705821,-1.3114729434,1.9321044426
C,0,-0.2608161449,-1.8700306698,-0.1194845617
H,0,0.3194401419,-2.1061590185,-1.0088382583
C,0,3.9396509962,-1.9306888797,0.0181414051
H,0,4.3231554235,-1.8216820417,1.037556506
C,0,1.8465893078,2.8662572814,0.4070446223
C,0,3.1511147002,3.0813097811,-0.3742063614
H,0,2.9693922985,3.8501600972,-1.1407049364
C,0,3.6884547292,1.818863845,-1.0672074024
H,0,3.0901178732,1.6330799911,-1.9651442264
H,0,4.7199402551,2.0228748044,-1.3974357721
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```
 C,0,4.2291305644,-0.670439982,-0.7992004198
 H,0,5.3177913666,-0.5758888031,-0.9189198274
 H,0,3.8039340023,-0.8072235584,-1.8039695749
 C,0,3.6474231506,0.5909705773,-0.1604199419
 H,0,4.1514232701,0.8062522213,0.7896784556
 H,0,2.5978046789,0.4001283369,0.077858754
 C,0,4.4852555859,-3.202435951,-0.6210764689
 H,0,5.567061402,-3.0682186372,-0.7554130511
 H,0,4.0479117781,-3.3067967286,-1.6235051334
 C,0,4.2052590641,-4.4547986517,0.214751306
 H,0,4.6170213964,-5.3506285455,-0.2650251432
 H,0,4.6527794832,-4.3636297954,1.2128928214
 H,0,3.1259503711,-4.5946178826,0.3405375607
 O,0,4.0916648076,3.5665093967,0.5962354477
 H,0,4.9172801049,3.7443516695,0.1208817977
 H,0,2.0676447653,2.2175503156,1.2639624674
 C,0,1.3090736034,4.2064546955,0.9527892591
 H,0,1.0482963948,4.8723078507,0.1202717297
 H,0,0.411537277,4.0502818892,1.5625201402
 H,0,2.0792813011,4.6877149802,1.5620578217
```

```
MacB_6+4_D2.out
E(RB3LYP) = -1311.18886847
```

```
Zero-point correction= 0.548604 (Hartree/Particle)
Thermal correction to Energy= 0.577109
Thermal correction to Enthalpy= 0.578053
Thermal correction to Gibbs Free Energy= 0.491122
Sum of electronic and ZPE= -1310.640265
Sum of electronic and thermal Energies= -1310.611759
Sum of electronic and thermal Enthalpies= -1310.610815
Sum of electronic and thermal Free Energies= -1310.697747
```

```
     E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 362.141 112.739 182.962
```

```
 C,0,-1.6111006794,-1.7136636959,-0.6201288745
 C,0,-2.5139746077,-1.8498515555,-1.7539231091
 C,0,-3.7720444682,-1.3691074753,-1.6892395271
 C,0,-4.3951169157,-0.7031061982,-0.487706339
 C,0,-3.9574409549,0.8073813466,-0.2774805572
 C,0,-2.6585581715,0.9150228665,0.4693438644
 H,0,-4.3825043724,-1.3872182127,-2.5925227949
```

```
H,0,-2.1243181587,-2.2191114875,-2.7014201335
H,0,-2.1060451683,-1.6768428905,0.3478579212
H,0,-4.1348344171,-1.2428923307,0.4298101026
H,0,-3.8230075021,1.2475335807,-1.2726633047
H,0,-2.6913286236,0.6383169692,1.5261627287
C,0,-5.179785041,1.4771570356,0.423953581
H,0,-4.9118086424,1.8933145612,1.4040124484
H,0,-5.5596999894,2.3056293898,-0.185171297
C,0,-5.9282940619,-0.6099515103,-0.5347854506
H,0,-6.249132323,-0.1962611368,-1.5012962139
H,0,-6.4252666836,-1.5739945743,-0.3845677767
C,0,-6.25822859,0.382675345,0.5775415955
H,0,-7.277383795,0.7892308313,0.4954588105
O,0,-6.1099071027,-0.3284828434,1.8114221636
H,0,-6.1857672325,0.3208326281,2.5271367676
C,0,-1.4946919221,1.1666514095,-0.1343001499
H,0,-1.5074222718,1.3620460253,-1.2048043733
C,0,0.9429262388,1.5794212102,-0.471024689
O,0,0.8513519264,1.4807995367,-1.6839869153
C,0,-0.1186111528,0.960799119,0.440558242
H,0,-0.016490025,1.3535451498,1.4571402216
C,0,1.62626,-0.8569075666,1.0113513626
O,0,2.0283497604,-0.5186325443,2.1082753074
O,0,2.3728909594,-1.4636268053,0.0710355575
C,0,0.1888981337,-0.6281173468,0.5705090295
H,0,-0.4106764883,-0.9174164972,1.4405065317
C,0,-0.316303386,-1.3531570782,-0.6374622781
H,0,0.2526968406,-1.2796670562,-1.5600090121
C,0,3.6875865619,-1.982906558,0.4511822314
H,0,3.7546349443,-1.9169444278,1.541089388
C,0,2.0840453366,2.3187669394,0.2100439762
C,0,3.3070154795,2.4365469493,-0.7070476008
H,0,2.9730646009,2.9287754724,-1.6322473239
C,0,3.9102065383,1.0733307192,-1.0705754019
H,0,3.1129763186,0.4342418544,-1.4599119284
H,0,4.6217355224,1.2097391287,-1.8995743348
C,0,4.7977538592,-1.1375286243,-0.171563563
H,0,5.7384310907,-1.5095049131,0.2554798125
H,0,4.8431242473,-1.3327886888,-1.2525041015
C,0,4.6369193885,0.3731238983,0.090611343
H,0,5.6172316589,0.8400754405,0.2346374803
H,0,4.0918566736,0.5167826529,1.0296012302
C,0,3.7130488925,-3.4403418962,0.0028220799
H,0,4.7061591475,-3.8427042959,0.244536337
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H,0,3.6104241084,-3.4712248592,-1.0901660945
C,0,2.6188324254,-4.2854833939,0.6627718221
H,0,2.6821492015,-5.3313235193,0.3406393462
H,0,2.7120746512,-4.25852755,1.756405231
H,0,1.6273993341,-3.9028718221,0.3946983194
O,0,4.2578953106,3.2617539823,-0.0236990957
H,0,5.0312338072,3.3381133059,-0.6030947343
H,0,2.3513623384,1.7787013725,1.1251405093
C,0,1.5405828068,3.7070164382,0.6192636644
H,0,1.2598151497,4.2789301036,-0.2737171142
H,0,0.6579746428,3.6118029161,1.2628131216
H,0,2.3182188513,4.2556461764,1.1562079605

MacB_CopeTS_D2.out
E(RB3LYP) = -1311.16493487

Zero-point correction= 0.545852 (Hartree/Particle)
Thermal correction to Energy= 0.574344
Thermal correction to Enthalpy= 0.575288
Thermal correction to Gibbs Free Energy= 0.488205
Sum of electronic and ZPE= -1310.619083
Sum of electronic and thermal Energies= -1310.590591
Sum of electronic and thermal Enthalpies= -1310.589646
Sum of electronic and thermal Free Energies= -1310.676730

```
      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 360.406 112.569 183.283
```

C,0,1.8383177812,1.7006954549,0.0009251322
C,0,2.6272660226,2.1881329664,-1.1001205544
C,0,3.939966811,1.8861462185,-1.233483851
C,0,4.5928758927,0.911654611,-0.3220303541
C,0,3.910327503,-0.5159914468,-0.478869251
C,0,2.601472243,-0.6428760956,0.2046719911
H,0,4.4891445179,2.2202222861,-2.1119265205
H,0,2.1108476795,2.7413413901,-1.883871086
H,0,2.3239894777,1.5907214167,0.9643962637
H,0,4.472466251,1.1962311513,0.7311116565
H,0,3.7709765758,-0.6880247848,-1.5524364881
H,0,2.6276568923,-0.5528474915,1.2914617991
C,0,5.0040915998,-1.5002448146,0.0553116275
H,0,4.7069288553,-1.9505116148,1.0102134412
H,0,5.1468759116,-2.3181257927,-0.6592728862

```
C,0,6.0715698735,0.5992295703,-0.5674642403
H,0,6.2350851023,0.3918335915,-1.634008325
H,0,6.7473292737,1.4023586198,-0.2572420861
C,0,6.30198277,-0.6741030393,0.2474083878
H,0,7.1929486533,-1.2287259646,-0.0816106675
O,0,6.4568671441,-0.2550101612,1.6064668017
H,0,6.5099140898,-1.0548388313,2.1516595543
C,0,1.4636644624,-1.1913381898,-0.3765209928
H,0,1.4461598457,-1.3021529471,-1.4600967207
C,0,-0.8836052272,-1.9435295199,-0.4790142864
O,0,-0.8592085398,-1.9946563913,-1.7087113833
C,0,0.2861378221,-1.4774216639,0.2876740257
H,0,0.2424376809,-1.5082452959,1.3713667641
C,0,-1.760759613,1.0471985788,1.0766532793
O,0,-2.3304258336,0.6432975145,2.0790978104
O,0,-2.393422258,1.5573734624,-0.0080050646
C,0,-0.2969447034,1.0583952109,0.9614900207
H,0,0.2010856914,0.7158531154,1.8620190647
C,0,0.4324260885,1.6619339198,-0.0297569538
H,0,-0.0835344047,1.9948379382,-0.9283234936
C,0,-3.7670174604,2.0258823644,0.1610123161
H,0,-3.9809356122,2.0174780579,1.2343202856
C,0,-2.0996339662,-2.4047549564,0.3247246158
C,0,-3.3217434693,-2.5467866705,-0.5911648452
H,0,-3.0171372597,-3.1755318837,-1.439395791
C,0,-3.8080437068,-1.1925218417,-1.1322008656
H,0,-2.940547868,-0.6181839059,-1.4703197058
H,0,-4.4270800401,-1.3612825684,-2.0268543232
C,0,-4.752497616,1.0991481227,-0.5459711077
H,0,-5.7530146191,1.4865140425,-0.311234949
H,0,-4.6256203727,1.1962405926,-1.6338163884
C,0,-4.623514346,-0.377000072,-0.1177080154
H,0,-5.6166234253,-0.8274185908,-0.0112534572
H,0,-4.1593850826,-0.4281615512,0.8722581355
C,0,-3.7968436694,3.4548634971,-0.3734795743
H,0,-4.8354030882,3.8087634758,-0.3225757872
H,0,-3.5157426746,3.4357111109,-1.4351367812
C,0,-2.8765172418,4.3993819408,0.4059104741
H,0,-2.9239864006,5.418670026,0.0049047454
H,0,-3.1641878222,4.4352060759,1.464842039
H,0,-1.8374637279,4.0553203876,0.3498598261
O,0,-4.3489933915,-3.2081331876,0.1603964825
H,0,-5.1159302573,-3.2877249579,-0.4267906829
H,0,-2.3039338385,-1.6627272443,1.1078234744
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 C,0,-1.7428771106,-3.7398835922,1.013489918
 H,0,-1.5261785529,-4.507566449,0.2597027844
 H,0,-0.8604627352,-3.6277072456,1.6544503855
 H,0,-2.5859295771,-4.0781359488,1.6209623772

MacB_Prod_Endo_2.out
E(RB3LYP) = -1311.20474203

Zero-point correction= 0.547700 (Hartree/Particle)
Thermal correction to Energy= 0.576765
Thermal correction to Enthalpy= 0.577710
Thermal correction to Gibbs Free Energy= 0.487846
Sum of electronic and ZPE= -1310.657042
Sum of electronic and thermal Energies= -1310.627977
Sum of electronic and thermal Enthalpies= -1310.627032
Sum of electronic and thermal Free Energies= -1310.716896

     E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 361.926 112.790 189.133

 C,0,-1.4357750495,-1.5603730891,-1.835297469
 C,0,-2.2743079154,-2.8104095921,-1.6480935117
 C,0,-3.4540926383,-2.8598219758,-1.0198744925
 C,0,-4.0696941925,-1.6211033307,-0.4372482706
 C,0,-2.9973289508,-0.5751463711,-0.1203325219
 C,0,-2.1698118721,-0.2387119192,-1.3588248254
 H,0,-3.9945448661,-3.802649052,-0.9484545079
 H,0,-1.8394212692,-3.7193317995,-2.0607444452
 H,0,-1.2448429107,-1.4312876812,-2.9106748369
 H,0,-4.743956672,-1.1785061734,-1.1908036126
 H,0,-2.3193725632,-1.0072249992,0.6305884878
 H,0,-2.8402061517,0.073757319,-2.1704548041
 C,0,-3.8229999617,0.5122887825,0.5692385666
 H,0,-3.2273955664,1.2660064618,1.0983892221
 H,0,-4.4518509675,1.0306805965,-0.1687058728
 C,0,-4.8540691406,-1.7178648428,0.8877740747
 H,0,-5.9021385249,-1.9971495074,0.7382774722
 H,0,-4.3963433814,-2.4548152123,1.5569359449
 C,0,-4.7018124499,-0.3146238125,1.5465386302
 H,0,-5.6765337616,0.1662352939,1.714264753
 O,0,-4.0347269469,-0.515983563,2.7941425061
 H,0,-3.9238480183,0.3553947666,3.2054649642
 C,0,-1.1964421499,0.8647965861,-1.0572345943
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H,0,-0.7172432301,0.787663775,-0.0836221127
C,0,0.1350922971,2.9227973531,-1.5904019814
O,0,0.5861521452,3.5961025833,-2.5099934027
C,0,1.5056355571,-2.2718563796,0.6271467978
O,0,1.683290755,-2.6389682162,1.772325433
O,0,2.4513864483,-1.6902404309,-0.1492971289
C,0,0.1999679771,-2.3689717761,-0.0684063464
H,0,-0.5485720265,-2.9779458918,0.4301487515
C,0,-0.0827037729,-1.6670342442,-1.1731198034
H,0,0.7015452983,-1.0522950236,-1.6061257548
C,0,3.6716826749,-1.1993902693,0.4687719326
H,0,3.5009509839,-1.1372599993,1.5490615896
C,0,0.5249707308,3.2224897005,-0.1440305823
C,0,2.0023098251,3.6192557442,-0.0326609548
H,0,2.1557293403,4.5190938529,-0.6448516444
C,0,2.9664692388,2.5256295127,-0.5160876901
H,0,2.850857112,2.4060753372,-1.6003432298
H,0,3.9939953815,2.886906493,-0.3495516036
C,0,3.9031795701,0.1891188366,-0.1247189631
H,0,4.8590887848,0.5729614475,0.2580568039
H,0,4.0136989876,0.0856545753,-1.2135907371
C,0,2.7794453026,1.1798852826,0.1929908363
H,0,2.7254011043,1.3502204645,1.2762079562
H,0,1.8234838784,0.7366054362,-0.1105811576
C,0,4.8142908248,-2.1685980438,0.1774817746
H,0,5.7264454268,-1.7384417773,0.6137253975
H,0,4.9677328772,-2.2079123531,-0.9098998526
C,0,4.5786864437,-3.5770711334,0.7312526959
H,0,5.4515385818,-4.2153396765,0.5487280736
H,0,4.3813035137,-3.5462559125,1.8083059228
H,0,3.7094088927,-4.0396728287,0.2519621937
O,0,2.2264008178,3.9144703618,1.3519003854
H,0,3.144225467,4.2160070609,1.4307774533
H,0,0.3649156557,2.3512306423,0.4960943583
C,0,-0.402649526,4.3537567916,0.3469177148
H,0,-0.2667596931,5.2427532625,-0.2805884441
H,0,-1.4536042696,4.0450839943,0.2898050163
H,0,-0.1558839256,4.6073416446,1.3812429075
C,0,-0.8710441047,1.8711802699,-1.880412799
H,0,-1.3060294251,1.9310546488,-2.8776206628
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