

DYNAMIC EFFECTS IN NUCLEOPHILIC SUBSTITUTION REACTIONS

A Dissertation

by

XAVIER SHELDON BOGLE

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

DOCTOR OF PHILOSOPHY

December 2011

Major Subject: Chemistry

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Chair of Committee,	Daniel A. Singleton
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ABSTRACT

Dynamic Effects in Nucleophilic Substitution Reactions.

(December 2011)

Xavier Sheldon Bogle, B.A., Franklin & Marshall College

Chair of Advisory Committee: Dr. Daniel A. Singleton

In order to rationally optimize a reaction, it is necessary to have a thorough understanding of its mechanism. Consequently, great effort has been made to elucidate a variety of reaction mechanisms. However, the fundamental ideas needed to understand reaction mechanisms are not yet fully developed. Throughout the literature, one encounters numerous examples of experimental observations that are not explainable by conventional mechanistic ideas and methods. The research described in this dissertation employs a unique approach towards the identification and analysis of systems whose observations cannot be explained by conventional transition state theory (TST).

The nucleophilic substitution of 4,4-dichloro-but-3-en-2-one by sodium-para-tolyl-thiolate was explored. It was deduced that the reaction was concerted and consequently, the product selectivity observed in the reaction cannot be explained by TST. Dynamic effects play a major role in the observed selectivity and this is further supported by the results of dynamic trajectory simulations.

Using computational studies, the ethanolysis of symmetric aryl carbonates was also shown to be concerted, provided that the substrate possesses good leaving groups.

Furthermore, extensive precedence has been set by Gutthrie, Santos, Schelgel, and others, detailing concerted substitutions at acyl carbon.

The Fujiwara hydroarylation is thought to occur by either a C-H activation mechanism or an electrophilic aromatic substitution (EAS). The KIEs associated with this reaction have been determined and provide strong support for the latter.

Computational studies also displayed fair agreement with experimentally determined KIEs, further supporting the EAS mechanism.

Isotopic perturbation of equilibria is invaluable in helping to determine whether a structure exists as a single structure or whether it is a time average of two equilibrating structures. The bromonium cation of tetramethylethylene and hydrogen phthalate have been wrongly reported as existing as equilibrating structures. The time averaged geometries have been determined in each case, via a variety of methods and the myth of equilibrating structures in the above cases has been debunked.

DEDICATION

TO MY FAMILY AND MY LOVELY WIFE DANA

ACKNOWLEDGEMENTS

I would like to thank my advisor, Dr. Singleton, for his guidance, patience, and support throughout my tenure as a graduate student under his tutelage.

I would like to thank my committee members, Dr. Bergbreiter, Dr. Connell, and Dr. Cagin, for their time and direction.

A special thanks to the past and current Singleton group members who have provided me a fruitful arena for learning and discussion; I am indebted to their friendship and encouragement. I am thankful for the many friends, acquaintances, and experiences that I have had so far in my career.

Finally, thanks to my mother, my father, my brother, and my sister, for their encouragement and to my wife for her patience and love.

NOMENCLATURE

B3	Becke 3-Parameter Exchange Model
GIAO	Gauge-Including Atomic Orbitals
LYP	Lee-Yang-Parr Gradient-Corrected Functionals
MPW1	Modified Perdew-Wang 1-Parameter Model
ONIOM	Our Own N-layered Integrated Molecular Orbital and Molecular Mechanics
PW91	Perdew-Wang 1991 Gradient-Corrected Functionals

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CHAPTER I

INTRODUCTION

The understanding and ultimately the control of chemical reactions are central goals of physical organic chemistry. In order to rationally optimize a reaction, it is necessary to have a thorough understanding of its mechanism. Consequently, great effort has been made to elucidate a variety of reaction mechanisms. However, the fundamental ideas needed to understand reaction mechanisms are not yet fully developed. Throughout the literature, one encounters numerous examples of experimental observations that are not explainable by conventional mechanistic ideas and methods. The research described in this dissertation employs a unique approach towards the identification and analysis of systems whose observations cannot be explained by conventional transition state theory (TST).

In its simplest form, a chemical reaction represents the conversion of reactants into a product. This conversion occurs by a particular reaction mechanism, which is most commonly viewed as a description of the path or sequence of steps leading to product formation. As will be seen, more information than this may be needed, but the determination of this path or sequence of steps in itself can prove challenging for a variety of reasons. Most often, the reactive intermediates formed en route to product have extremely short life times thereby making their observation impractical. In others, one may encounter reactions that have overlapping, competing rate-limiting steps that

This dissertation follows the style of *Journal of the American Chemical Society*.

fluctuate based on external factors such as concentration, temperature or pH of the reaction medium.

As defined by TST, the selectivity observed between two products in a reaction is directly related to the relative free energies of the transition states (TSS) of the competing pathways. However, in stark contradiction to this idea, there are documented cases where only a single transition structure is locatable but yet two distinct products are formed.¹ Under these circumstances, TST is incapable of qualitatively accounting for the experimental observations and it will be shown that these systems are instead controlled by a type of “dynamic effect” where the decision to form either product is made on the downward slope on a bifurcating energy surface after passing through the transition state. Essentially, trajectories (reaction paths from starting material to product) on these bifurcating surfaces can pass through the first transition state and afford the products without passing through any successive intermediates or transition states.

As tools, the work in this dissertation will use the determination of experimental kinetic isotope effects (KIEs) using the Singleton natural abundance methodology,² dynamic trajectory studies, theoretical KIE predictions and kinetic rate studies. These mechanistic probes are employed in conjunction with each other to determine the structural features of transition states, identify rate limiting or product determining steps and the elucidation of overall mechanisms. It should be noted that this dissertation will not describe the intricacies of the Singleton natural abundance NMR methodology as it has been described in numerous dissertations and publications.

Kinetic Isotope Effects

The substitution of one isotope for another at or near an atom in which bonding changes are occurring generally leads to small changes in the observed rates. These small changes in the observed rates are termed kinetic isotope effects and they originate mainly from the difference in frequencies of the vibrational modes of two isotopologues.

The frequency of a stretching vibration is modeled by the classic equation (eqn. 1-1) for the stretching of a spring with masses at both ends. The reduced mass of a bond between a heavy atom (C, N, and O) and H is significantly affected upon substitution of H by D. The reduced mass, m_r , increases, subsequently causing the stretching frequency and the zero-point energy (ZPE) of a C-D bond to be lower than that of a C-H bond.

$$\nu = 1/2\pi (k/m_r)^{1/2} \quad m_r = m_1m_2/m_1+m_2 \quad (1-1)$$

As illustrated in Figure 1-1, an isotope effect is observed for a C-H vs C-D bond when the levels of the ZPE associated with each isotope, change to different extents on proceeding from starting materials to the transition state. If the normal modes are closer in energy at the transition state than they are in the starting material, a decrease in ZPE is observed and the lighter isotope encounters a smaller activation barrier. In this case, lighter isotopes tend to react faster and this is referred to as a normal isotope effect. In the opposing case, where the normal modes are further apart in the transition state vs. starting materials, then the heavier isotope has a lower barrier to overcome and consequently reacts faster than the lighter isotope. This isotope effect is called an inverse

isotope effect. It should be pointed out that factors other than ZPE play some role in KIEs when conventional TST is considered, but ZPE is usually the dominant contributor to the isotope effect.

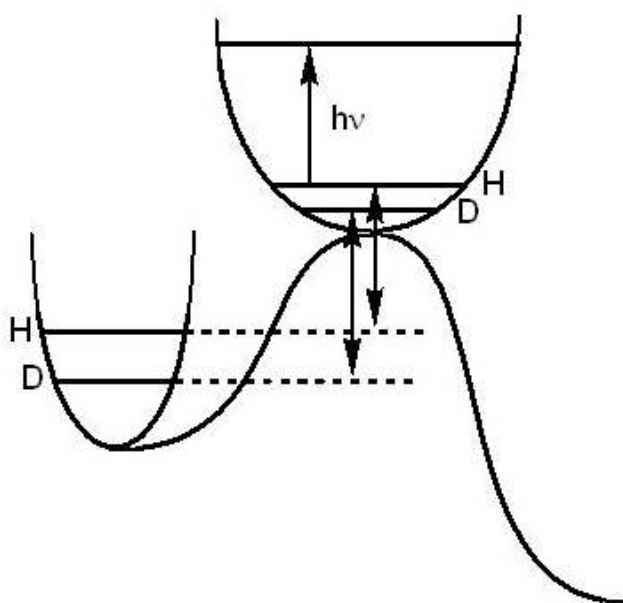


Figure 1-1. Origin of a Kinetic Isotope Effect. They result from changes in the ZPE on going from starting materials to the transition state.

Traditional isotope effect studies require explicit isotopic labeling at all positions for which an isotope effect will be determined. This is often an arduous task and as such these methods can prove to be somewhat limited and highly inefficient. All of the KIEs reported in this dissertation were determined at natural abundance using the Singleton methodology.² This methodology takes advantage of the competition reaction that is inherent between isotopes at their natural abundances, and avoids all difficulties

associated with the synthesis of labeled materials. As a reaction proceeds to high conversion, the product becomes enriched in the faster reacting isotopologues while the starting material becomes enriched in the slower reacting isotopologues. A comparison is then made between the isotopic content of the recovered starting material and that of original material that hasn't been exposed to reaction conditions. The KIE is then determined from this comparison.

Dynamic Effects

Transition state theory is the underlying paradigm by which chemists understand reactivity and selectivity. However, in recent years, the Singleton group has shown that there are numerous instances encountered in studying simple organic reactions where TST proves incapable of accounting for experimental observations. Under these circumstances, an alternate approach has to be taken which involves taking the impact of the collective momenta and motion of atoms on the observed experimental outcomes into account. This impact of the momenta and motion of atoms on the experimental outcomes is what we call a dynamic effect.

There are several different types of dynamic effects that have been identified in chemical reactions. Carpenter has been studying the phenomenon of dynamic matching since 1984.³ One assumption generally made is that intramolecular vibrational energy redistribution (IVR) is fast relative to the timescale of the reaction. This is not always the case and consequently the passage of trajectories passing through an initial transition state can influence the selectivity among successive transition states. Based on this

dynamic matching effect, TST based methods fall short of accurately predicting experimental results and instead, dynamic trajectories have to be employed to make accurate predictions of the selectivity.⁴

A second type of dynamic effect that is also due to slow IVR is non-statistical recrossing. Recrossing occurs when a trajectory passes the transition state, runs into a potential energy wall and then reverts to starting material instead of forming product. To some extent, statistical versions of TST such as microcanonical variational TST, are capable of reasonably predicting and allowing for recrossing.⁵ However, it is also known that some recrossing that occurs is not statistically predictable.

Singleton and Ussing first demonstrated non-statistical recrossing experimentally in the cycloaddition of diphenyl ketene and cyclopentadiene as depicted in Figure 1-2.⁶ Here the first step of the mechanism is the formation of a bond between C α and C1. The trajectory passes TS **3** and then continues toward **4**, which is the TS by which **5** and **6** can interconvert. Basically, in most cases, C α and C1 approach each other, fail to form a bond and return to starting materials via TS **3**. The key result from this study is that the rate of the reaction was not determined by **3** and the experimental KIEs reflect **4**, which is well beyond the statistical TS.

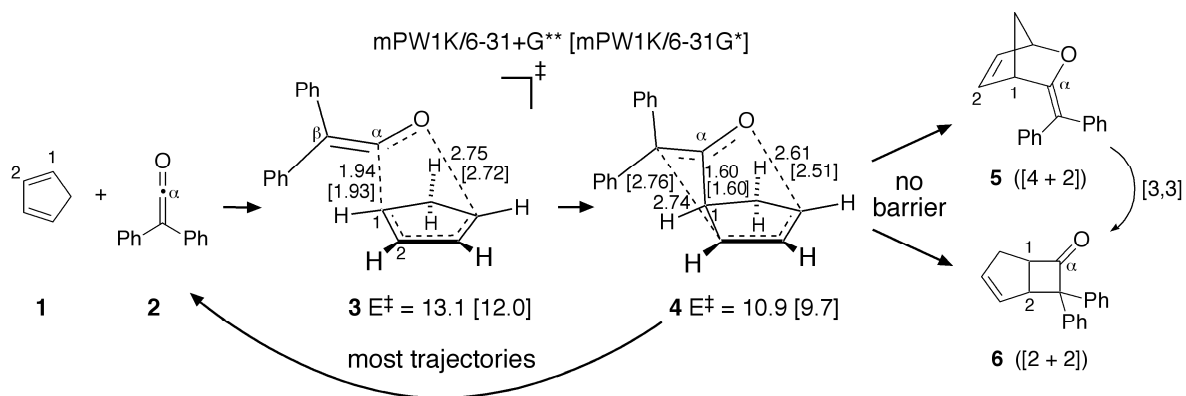


Figure 1-2. Cycloaddition of Cyclopentadiene and Diphenylketene.

A third type of dynamic effect, and the one that has most significance to this dissertation, is associated with bifurcating potential energy surfaces. Chemists generally assume that separate products are the result of separate transition states and the respective ratios of these products are directly related to the relative energies of the competing transition states. However, it has also been recognized that this assumption may be unreliable.⁷

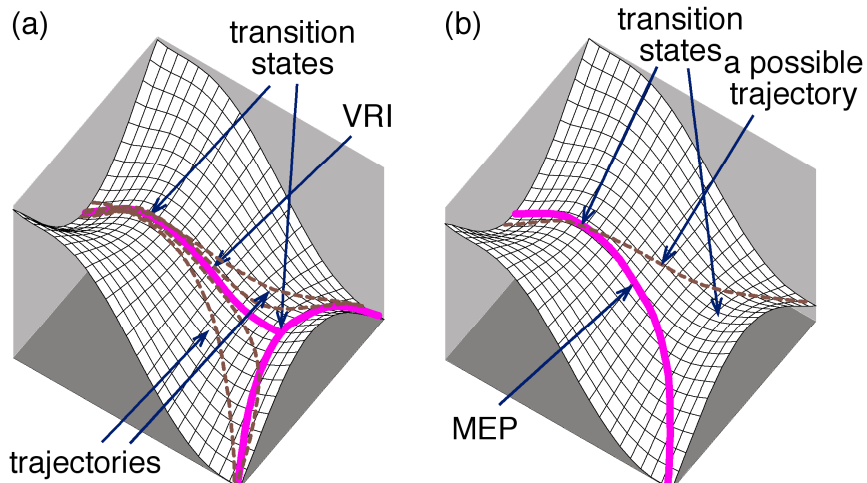


Figure 1-3. Symmetrical and Unsymmetrical Potential Energy Surfaces. (a) The surface is symmetrical and the minimum-energy path (MEP) bifurcates at a second transition state. Trajectories would tend to diverge from the MEP in the area of the valley-ridge inflection (VRI). (b) The surface is unsymmetrical and the MEP does not bifurcate.

Figure 1-3 depicts two types of bifurcating surfaces where reactants can first pass through the initial TS and then proceed to product without barrier. In Figure 1-3(a), a symmetrical bifurcating surface is depicted where the minimum energy pathway (MEP) bifurcates to give, equally, two equivalent products.⁸

Figure 1-3(b) is far less understood and provides a more interesting case where the bifurcating surface is now unsymmetrical and trajectories may lead to two, distinguishable products.⁹ The MEP no longer bifurcates and as a result, TST cannot predict the experimental product ratios.¹⁰ As will be shown in Chapter III, dynamic trajectories are the only way of accurately predicting product ratios in these systems where the energy surface is unsymmetrical.

Taking the evidence presented into account, as well as the results that will be presented in the following chapters, it will become apparent that the utilization of the Singleton methodology to determine experimental KIEs, prediction of theoretical KIEs, kinetic rate studies and dynamic trajectories are highly efficient mechanistic probes. Furthermore, when used in conjunction, they provide the ability to show that dynamic effects are prevalent in simple organic reactions such as nucleophilic substitutions.

CHAPTER II

ETHANOLYSIS OF SYMMETRIC ARYL CARBONATES

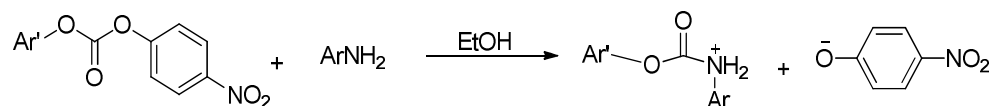
Introduction

Nucleophilic substitution at acyl carbons is undoubtedly one of the cornerstone transformations in organic chemistry. Many synthetically useful products and intermediates can be accessed via this route and consequently, these transformations have been explored extensively throughout the literature. The conventional mechanism for nucleophilic substitution at acyl carbon involves a stepwise addition-elimination process proceeding through a tetrahedral intermediate. However, in numerous cases, experimental or computational studies have supported the significance of the concerted pathway, particularly in reactions involving substrates with good leaving groups.¹¹ There has been a recurring debate over whether the concerted reactions are relatively common or only occur under exceptional circumstances.

In the 1950's Bender¹² employed ¹⁸O labeling experiments to provide compelling evidence for the tetrahedral intermediate in the hydrolysis of several carboxylic esters. However, the generality of the tetrahedral intermediate was later questioned when Bender et al.¹³ reported the lack of ¹⁸O incorporation during alkaline hydrolysis of benzyl benzoates. McClelland performed rate studies on the breakdown of an anionic hemi-ortho ester and concluded that for leaving groups better than alkoxide, the lifetime of the tetrahedral intermediate would be too short to exist.¹⁴ Williams et al. explored the attack of phenoxide on 4-nitrophenylacetate and found that the Brønsted dependence for

this process was linear and hence was inconsistent with a mechanism involving a tetrahedral intermediate.¹⁵

Santos and Castro et al. have extensively explored the nucleophilic attack of amine nucleophiles on substituted aryl carbonates as depicted in Figure 2-1.¹⁶ They employed an approach similar to that which McClelland used by performing kinetic studies with different substrates, obtaining Brønsted plots and using a combination of the slopes associated with each plot and results from earlier studies¹⁷ to determine the nature of the mechanism. Ultimately, a connection was established between leaving group ability and the likelihood of concertedness i.e. the better the leaving group, the more likely the reaction is to occur in a concerted fashion.



Ar' = 4-methylphenyl and 4-chlorophenyl; anilinolysis is stepwise

Ar' = 4-nitrophenyl, anilinolysis is concerted

Figure 2-1. Anilinolysis of Substituted Aryl Carbonates.¹⁶

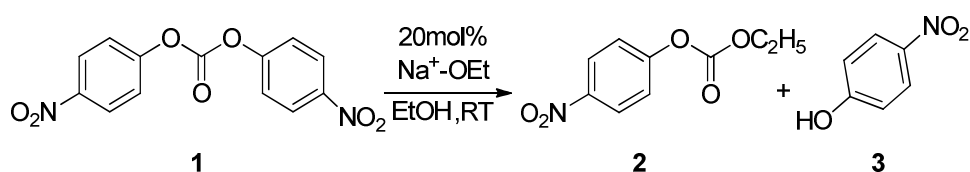
Reactions proceeding via a concerted mechanism are particularly interesting in that any observed leaving group selectivity may be determined by dynamic effects. The potential energy surface that defines the nucleophilic attack of a symmetric aryl carbonate is a symmetric one.

In this chapter, we will detail the exploration of the ethanolysis of symmetric aryl carbonates. Based on the evidence provided earlier, this reaction is hypothesized to

occur in a concerted fashion. A combination of ^{13}C , ^{17}O intermolecular KIEs and dynamic trajectory simulations will be employed to test the hypotheses and show that dynamic effects play a role in the observed selectivity.

Results

The reaction of bis-para-nitrophenyl carbonate and sodium ethoxide was chosen for analysis. This carbonate substrate was chosen because it has several key characteristics. Firstly, it possesses two para-nitrophenoxide leaving groups and as outlined by Santos et al. the presence of the nitro groups serve to destabilize the potential tetrahedral intermediate to such an extent that the mechanism is likely to be concerted.¹⁷ Secondly, this substrate presents an excellent opportunity for us to probe the mechanism by determining the ^{17}O intra-molecular isotope effect associated with the reaction. The ^{17}O KIE was expected to be indicative of a concerted versus stepwise process.



One additional area of concern regarding the kinetics of this mechanism was the overall mode of base catalysis at work in the reaction. A specific base catalyzed process would display fairly simple kinetics while a general base catalyzed process would most

likely be mechanistically ambiguous.¹⁸ This mechanistic ambiguity originates from the fact that the reaction generates para-nitrophenoxide as a product, which could also function as a basic species.

This was addressed by performing a kinetic study in which uniform aliquots were removed at specific time intervals and analyzed by ¹H NMR to determine the overall conversion of the reaction. This was then plotted versus time to determine whether the reaction rate was constant or whether it decreased over time. As evidenced in Figure 2-2, the overall rate of the reaction decreases as the reaction progresses and thus, is suggestive of a specific base catalyzed process.

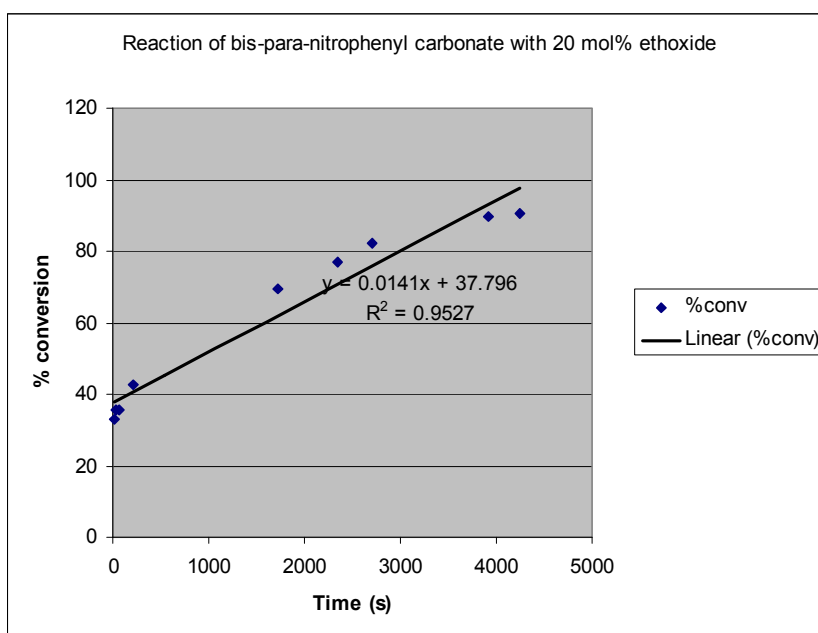


Figure 2-2. Kinetic Study of the Reaction of **1** with Sodium Ethoxide.

Intermolecular ^{13}C KIEs of Bis-para-Nitrophenyl Carbonate

The intermolecular KIEs for the reaction of **1** with sodium ethoxide in anhydrous ethanol are expected to provide important information regarding the transition state of the rate limiting step. The intermolecular ^{13}C KIEs for the ethanolysis of bis-para-nitrophenyl carbonate were determined at natural abundance using the Singleton NMR methodology.¹⁹ Two ethanolysis reactions catalyzed by 2 mole percent sodium ethoxide in anhydrous ethanol at 25 °C were taken to $82 \pm 2\%$ conversion and $74 \pm 2\%$ conversion (determined by ^1H -NMR), quenched, and unreacted starting material was recovered following an aqueous workup and column chromatography. In each case, the ^{13}C composition at each position in the recovered samples was determined using the Singleton ^{13}C -NMR methodology and compared to ^{13}C composition of standard samples that were not subjected to reaction conditions. The relative ^{13}C compositions were determined by using the carbons ortho to the nitro group as an internal standard, with the assumption that their individual isotopic compositions remained constant throughout the reaction. The intermolecular KIEs so determined are listed in Figure 2-3.

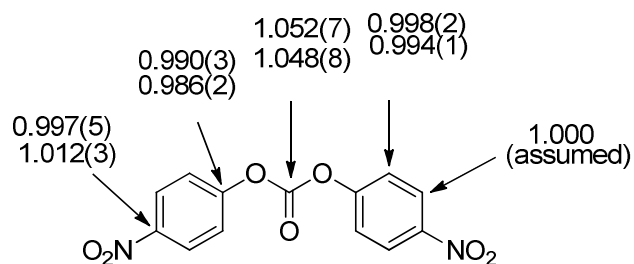


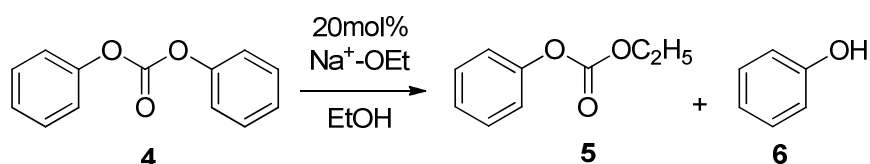
Figure 2-3. Intermolecular ^{13}C KIEs ($k^{12}\text{C}/k^{13}\text{C}$) for the Ethanolic Hydrolysis of **1**. Both sets of KIEs represent two independent experiments with the standard deviations listed in parentheses.

One issue that surfaced during the analysis was the fact that **1** was not sufficiently soluble in common deuterated solvents at room temperature. This issue was avoided by both heating the probe to 60 °C in deuterated acetonitrile to maximize homogeneity and reducing the amount of sample used to ~300mg to prevent “crashing out” during analysis. This occurred quite frequently when larger amounts of material (~500 mg) were used.

The main observation here is that a large primary isotope effect is observed for the carbonyl carbon, which is consistent with both our expectations and with earlier results published by O’Leary et al. for the hydrolysis of aryl carbonates.²⁰ However, the carbon atoms at quaternary positions appeared to exhibit isotope effects which were contrary to our predictions. These unexpected KIEs on the quaternary carbons were hypothesized to be a result of peak broadening brought on by the increased temperature necessary to maintain homogeneity and minimize viscosity of the sample. This called into question the complete set of results obtained with **1**.

Intermolecular ^{13}C KIEs of Diphenyl Carbonate

To address the solubility/viscosity issue encountered during the analysis of bis-para-nitrophenyl carbonate, the decision was made to try a new substrate, diphenyl carbonate **4**, bearing in mind that this new substrate still met the required criteria. It possessed two good leaving groups and thus was still likely to react in a concerted manner and was also symmetric, which signified that an ^{17}O intra-molecular analysis was still viable.



In a much similar fashion to before, two reactions were taken to $81 \pm 2\%$ conversion and $77 \pm 2\%$ conversion, quenched, and unreacted starting material was recovered following an aqueous workup and column chromatography. The increased solubility of diphenyl carbonate relative to bis-para-nitrophenyl carbonate afforded us the ability to use deuterated chloroform as our solvent which was desirable from a familiarity standpoint. In addition, this also meant that high probe temperatures were no longer necessary and subsequent NMR analyses were instead run at a probe temperature of $40\text{ }^\circ\text{C}$. It was hypothesized that this would help to circumvent the issues plaguing the previous analysis of bis-para-nitrophenyl carbonate. Apart from the above mentioned changes, the isotopic analysis was carried out in a much similar manner to that of the

nitro substituted analog and the isotope effects so determined are listed in Figure 2-4.

The observation that the KIEs for the phenyl rings approached unity and that the sets of KIEs are consistent supports the success of the analysis.

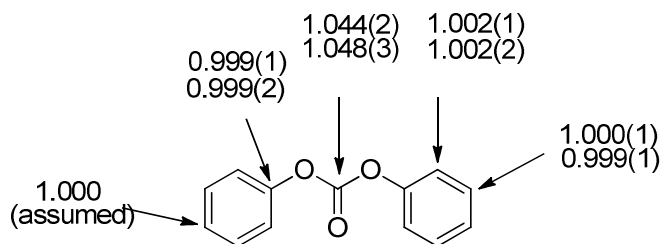


Figure 2-4. Intermolecular ^{13}C KIEs ($k^{12}\text{C}/k^{13}\text{C}$) for the Ethanolysis of Diphenyl Carbonate. Both sets of KIEs represent two independent experiments with the standard deviations listed in parentheses.

Again, the KIE calculated for the carbonyl carbon is consistent with that observed in the literature. In addition, this study also provides answers regarding the appearance of unexpected KIEs that were observed for the quaternary carbons of bis-para-nitrophenyl carbonate. In Figure 2-4, all aromatic carbons, quaternary carbons included, have KIEs that are essentially unity or within experimental error of unity. Qualitatively, this indicates that there is very little bonding of the nucleophile, if any, to these aromatic carbons at the rate limiting transition state. By directly comparing the KIEs listed in Figure 2-4 with those of bis-para-nitrophenyl carbonate listed in Figure 2-3, then it becomes apparent that the “phantom” KIEs observed on the quaternary carbons are directly related to the homogeneity/viscosity issues that were encountered with the analysis of that sample.

Intramolecular ^{17}O KIEs of Diphenyl Carbonate

As was alluded to earlier, the symmetric nature of the carbonate species being studied provides a unique opportunity to probe the mechanism of the ethanolysis using intramolecular ^{17}O isotope effects. Unlike intermolecular KIEs which define the transition state of the rate determining step, intramolecular kinetic isotope effects are a reflection of the nature of the transition state of the selectivity determining step. This isotope effect originates from the fact that isotopic substitution in either oxygen alpha to the carbonyl group of the carbonate substrate induces desymmetry and ultimately an isotope effect represents the choice between an ^{17}O or ^{16}O being expelled to give a non-statistical distribution of isotopomeric products.

Under normal circumstances, conventional intramolecular KIE studies would be performed on recovered product but in this system, the mono-substituted product can potentially react with a second ethoxide molecule to form the disubstituted product. Hence, determining the isotope effect from recovered product was not feasible as there would also be an isotope effect associated with the second substitution.

The intramolecular analysis was carried out in a much similar manner to the intermolecular study on diphenyl carbonate. The only difference was that, this study was run at twice the scale of the previous to account for a second reaction that was necessary to generate the standard for the NMR analysis.

As outlined in Figure 2-5, the first ethanolysis reaction was taken to high conversion and generated phenol that was designated as the “sample” for ^{17}O analysis. The monosubstituted product, ethyl phenyl carbonate, was then isolated using flash

column chromatography and reacted again to generate the ^{17}O standard sample. Since intramolecular KIEs represent the competition between two branches of a mechanism that are equivalent, not considering isotopic substitution, then it becomes apparent why there may be an isotope effect in the first reaction but none in the second. Ultimately, the presence of an ^{17}O intramolecular isotope effect would be indicative of a concerted process.

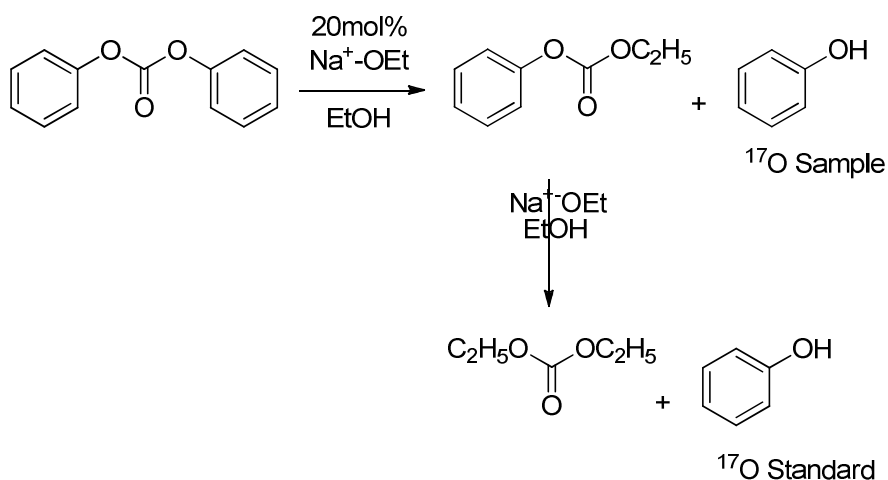


Figure 2-5. Reaction Schematic for Determination of ^{17}O KIEs.

However, in practice, the low sensitivity of ^{17}O nucleus coupled with its strong tendency for broad peaks proved to be obstacles too great to be overcome with the current resources at our disposal.

Theoretical Studies

Initially, gas phase DFT calculations (B3LYP/6-31G*) were employed to model the potential energy surface representing the ethanolysis of both **1** and **4** and also to locate the transition states associated with each system. However, there was some skepticism whether these gas phase methods would be capable of accurately representing the potential energy surface for these reactions in solution.

Predicted Isotope Effects

The ^{13}C KIEs were calculated for the addition transition state of **1** with methoxide (**TS1**) and the corresponding transition state of **4** with methoxide (**TS2**) using the Bigeleisen-Mayer method.^{21,22} In both cases it was assumed that the use of methoxide would have no effect on the overall geometry of the TS and consequently no effect on the theoretically determined KIEs.

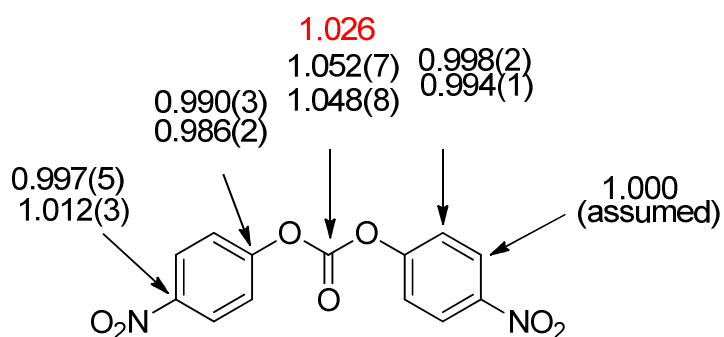


Figure 2-6. Predicted KIEs (red) for the Ethanolysis of **1**. Experimentally determined KIEs (black) also listed.

Upon analyzing both Figure 2-6 and Figure 2-7, it becomes apparent that the gas phase transition states from which the KIE predictions were made significantly underestimate the KIE determined from experiment. Consequently, we hypothesized that an alternate approach was needed that would account for the effect of solvent on the charged species in solution.

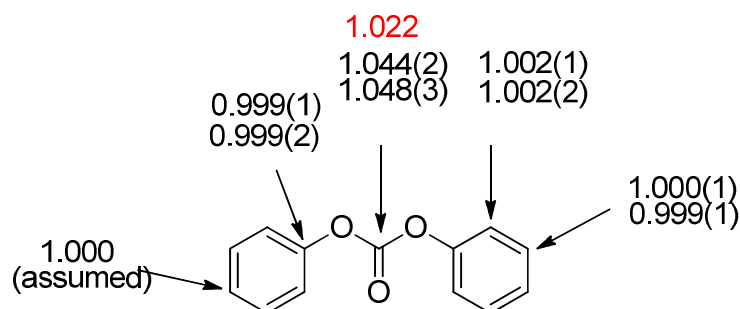


Figure 2-7. Predicted KIEs (red) for the Ethanolysis of **4**. Experimentally determined KIEs (black) are also listed.

ONIOM Method for Modeling Explicit Solvent Molecules

The ONIOM (Our own N-layered Integrated molecular Orbital and molecular Mechanics) method allows for the combination of much more powerful/computationally expensive *ab initio* methods and less expensive molecular mechanics methods in the same calculation with high levels of accuracy.²³ With regards to the carbonate systems being modeled, B3LYP/6-31G* *ab initio* method was used for the core atoms while an AM1 method was utilized for the 18 explicit solvent (ethanol) molecules surrounding the core.

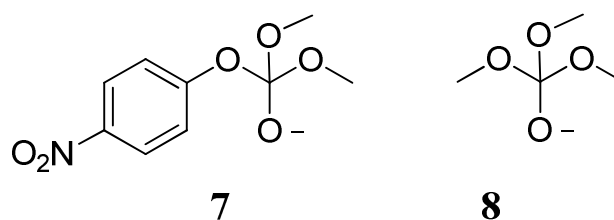


Figure 2-8. ONIOM Trajectories from Simplified Structures.

Dynamic trajectory simulations were initiated from both a simplified dimethoxy-para-nitrophenoxy methoxide core **7** as well as from the trimethoxy methoxide **8** as depicted in Figure 2-8, both of which were surrounded by 18 ethanol molecules. Interestingly, all trajectories that were initiated from **7** resulted in the expulsion of the nitrophenoxy group. This observation was indicative of the absence of an intermediate on the PES and as a result, represents a concerted reaction. Conversely, those initiated from **8** did not result in expulsion of any of the methoxy groups. This result was consistent with expectations as substrates with poorer leaving groups would be expected to react via a stepwise mechanism. Accordingly, trajectories initiated from **8** do not form a product because they instead oscillate in a minimum on the PES, the intermediate.

Discussion

Despite being unable to experimentally measure ^{17}O intramolecular isotope effects, the computational aspect of this work provided valuable insight into the nature of these reactions. Computationally, strong arguments can be made for the ethanolysis of aryl carbonates being concerted. ONIOM trajectories initiated from **7** and **8** provided strong support for the substitution reactions of aryl carbonates being concerted. The

results from the trajectories align well with experimental evidence provided by Bender, and Santos et al.; which showed that nature of the mechanism was directly related to the nucleofugality of the groups present. Substrates with good leaving groups are most likely to react in a concerted manner and exhibit selectivities that are determined by dynamic effects. Those with poorer leaving groups are more likely to do so in a stepwise fashion via a tetrahedral intermediate.

Experimental Section

General

All reactions were carried out in oven dried glassware and in most cases; freshly purified, dry solvents were used. All chemicals used were obtained commercially and 4.5 Å molecular sieves were added to solvents to maintain dryness when necessary. The reaction vessels were purged with N₂ prior to use.

Bis-para-Nitrophenyl Carbonate.²⁴ In 500 mL of toluene at room temperature, 6.030 g (30 mmol) of para-nitrophenyl chloroformate and 5.004 g (36 mmol) of para-nitrophenol were dissolved and stirred. Upon dissolution of the solids, 4.5 mL (36 mmol) of N,N-dimethylaniline was then dissolved in 70 mL of toluene and added dropwise to the reaction mixture via an addition funnel over a 15 min period. The reaction was allowed to run for 3 h and was then quenched with 250 mL of H₂O. The toluene layer was then washed with 3 x 250 mL portions of 5% HCl followed by 3 x 250 mL of 10% NaCl solution and finally 3 x 100 mL portions of 10% NaHCO₃ solution.

The remaining organic layer was concentrated under reduced pressure to give a white solid. This white solid was purified via recrystallization from CHCl_3 . The crystals so formed were then washed with a cold solution of 9:1 hexanes:ethyl acetate. The pure crystals were then allowed to air dry and trace amounts of solvent were then removed in vacuo. The overall yield was 73% (6.68 g isolated): ^1H NMR (CDCl_3) δ 8.33 (m, 4H) 7.51 (m, 4H); ^{13}C (CD_3CN) δ 156.17, 151.19, 147.04, 126.38, 123.07.

Intermolecular KIE Determination in the Ethanolysis of Bis-para-nitrophenyl Carbonate: Example Procedure. While stirring under N_2 , 5.005 g (16.5 mmoles) of bis-para-nitrophenyl carbonate was added to 2 L of anhydrous ethanol and allowed to stir at 25 °C until the solution was completely homogenous. To 10 mL of anhydrous ethanol was added 0.227 g (3.3 mmoles) of NaOEt and the solution was carefully warmed using a heat gun until homogeneity was achieved. The solution was then added quickly using a syringe to the 2 L ethanol/carbonate mixture. The reaction was monitored by NMR analysis of aliquots and was quenched after 45 mins with 5% HCl solution. The overall conversion was 82% and was computed by first integrating all the aryl protons and then deducing the relative integration for a single proton in each compound. The reaction mixture was then extracted with toluene, dried over CaSO_4 , filtered and then concentrated on a rotary evaporator. The unreacted starting material was then isolated from the concentrated reaction mixture by flash column chromatography using a 4:1 mixture of hexanes and ethyl acetate as an eluent. The fractions containing pure starting material were then concentrated under reduced

pressure to afford 400 mg of bis-para-nitrophenyl carbonate. An analogous reaction using 5.006 g of bis-para-nitrophenyl carbonate was taken to 74% conversion and 331.8 mg of pure starting material was isolated.

Intermolecular KIE Determination in the Ethanolysis of Diphenyl

Carbonate: Example Procedure. While stirring under N₂, 10.01 g (47 mmoles) of diphenyl carbonate was added to 2 L of anhydrous ethanol and allowed to stir at 25 °C until the solution was completely homogenous. To 30 mL of anhydrous ethanol was added 0.6423 g (9.4 mmoles) of NaOEt and the solution was carefully warmed using a heat gun until homogeneity was achieved. The solution was then added quickly using a syringe to the 2 L ethanol/carbonate mixture. The reaction was monitored by H-NMR analysis of aliquots and was quenched after 130 mins with 5% HCl solution. The overall conversion was 81% and was calculated in a similar manner to that used for **1**. The reaction mixture was then extracted with toluene, dried over CaSO₄, filtered and concentrated on a rotary evaporator. The unreacted starting material and ethyl phenyl carbonate product were then isolated from the concentrated reaction mixture by flash column chromatography using a 9:1 mixture of hexanes and ethyl acetate as an eluent. The mixture of carbonates was concentrated under reduced pressure and then chromatographed again using a 1:1 mixture of CH₂Cl₂ and hexanes. The fractions containing pure starting material were then concentrated under reduced pressure to afford 520 mg of diphenyl carbonate: ¹H NMR (CDCl₃) δ 7.42-7.36 (m, 4H) 7.26-7.23 (m, 6H); ¹³C (CDCl₃) δ 151.90, 151.07, 129.46, 126.11, 120.79. An analogous reaction

using 9.99 g of diphenyl carbonate was taken to 77% conversion and 376 mg of pure starting material was isolated.

Intramolecular KIE Determination in the Ethanolysis of Diphenyl

Carbonate: Example Procedure. While stirring under N₂, 10.00 g (47 mmol) of diphenyl carbonate was added to 2 L of anhydrous ethanol and allowed to stir at 25 °C until the solution was completely homogenous. To 60 mL of anhydrous ethanol 0.6420 g (9.4 mmol) of NaOEt was added and a heat gun was used to carefully warm the solution until homogeneity was achieved. A syringe was then used to quickly add the solution to the 2 L ethanol/carbonate mixture. The reaction was monitored by NMR analysis of aliquots and was quenched after 135 mins with 5% HCl solution. The overall conversion was 81%. The reaction mixture was then extracted with toluene, dried over CaSO₄, filtered and then concentrated on a rotary evaporator. The unreacted **4** and ethyl phenyl carbonate product **5** were then isolated from the concentrated reaction mixture by flash column chromatography using a 9:1 mixture of hexanes and ethyl acetate as an eluent to separate them from the phenol yielding 6.16 g mixture of **4** and **5**.

CHAPTER III

DYNAMIC CONTROL OF STEREOSELECTIVITY IN A NUCLEOPHILIC SUBSTITUTION REACTION

Introduction

Many forms of nucleophilic substitution reactions are intrinsically stereospecific, in that their products are defined in their mechanisms by the stereochemistry of the starting materials. Others are stereoselective, in that their product stereochemistry is defined by the choice among pathways leading to stereoisomeric products. The normal assumption in the latter case is that the stereoselectivity is determined by the free energies of competitive transition states leading to the products. We describe here how stereoselectivity in nucleophilic substitutions at sp^2 carbons can be decided by dynamic effects on the downhill slope of “bifurcating energy surfaces.”

The conventional mechanism for nucleophilic substitution at sp^2 carbons involves a stepwise addition-elimination process proceeding through a tetrahedral intermediate. In some reactions, however, experimental and computational studies have supported the importance of concerted substitutions, particularly when the reaction involves good leaving groups.

Williams showed that nucleophilic substitution reactions at acyl carbons can occur via a concerted mechanism contrary to the more conventional stepwise, addition-elimination process.²⁵ This was demonstrated in a series of reactions involving phenolate ions and various substituted 2-Aryloxazolin-5-ones. Utilizing a combination of kinetic

studies (rate and equilibrium constant determination) and ^{18}O labeling experiments; Williams et al. arrived at results that were consistent with a concerted displacement mechanism.

Castro and Santos have shown that a variety of acyl substitution can occur in a concerted fashion.^{26, 27, 28} They explored the nucleophilic attack of amine nucleophiles on substituted aryl carbonates and ultimately established a connection between the nucleofugality and the nature of the mechanism. Again, the better the leaving group, then the more likely the reaction to be concerted, as was discussed in Chapter II.

A theoretical basis for concerted mechanisms was established by Guthrie using multidimensional Marcus theory, and he particularly defined structural conditions under which substitutions are likely to be concerted.²⁹ This involved the initial derivation of equations permitting the application of Marcus theory to reactions with two, three or four reaction coordinate dimensions, based on the quartic approximation to the reaction coordinate (Eqn 3-1). Ultimately, Guthrie mapped the multidimensional hyperspace, searched for transition states on these surfaces and then determined the nature of the mechanism associated with a particular transition state depending on what the values (ranging from 0-1) of the reaction coordinates were at the transition state.

$$G=ax^2 + bx^3 + cx^4 \quad (3-1)$$

Schlegel and Bach studied nucleophilic substitutions on vinylic chlorides in the gas phase and established the viability of a concerted mechanism, though they suggested that the presence of electron-withdrawing groups could favor a stepwise process.³⁰

We considered that the concerted mechanism could lead to an intriguing phenomenon in the nucleophilic substitution reactions of electrophiles containing two leaving groups, such as carbonates or vinylic dihalides. When there are two leaving groups in a stepwise mechanism, the selectivity between leaving groups is decided by the relative energies of the competing transition states for loss of the leaving groups. For a concerted process, however, it seemed possible that the reaction could involve only a single transition state that is passed through before the structural “decision” has been made as to which of the two leaving groups will be lost. In such a circumstance, the selectivity between leaving groups, and the product selectivity, could be decided by dynamic effects on the slope of the potential energy surface beyond the transition state.

Results

To explore this possibility, nucleophilic substitution on the dichlorobutenone **1** was chosen for study. In **1**, the good chloride leaving groups should promote a concerted mechanism, based on the ideas expressed by Guthrie. In addition, reactions of **1** exhibit a stereoselectivity that is readily observable.³¹ The particular reaction of **1** with sodium para-tolylthiolate proved convenient, occurring rapidly in dry ethanol at 25 °C.

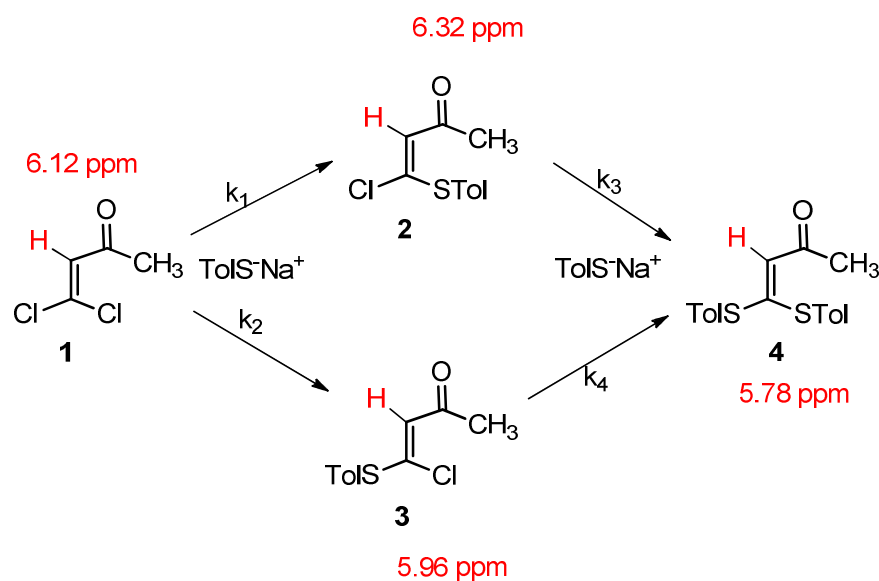


Figure 3-1. Reaction of **1** with Sodium Para-tolylthiolate. H-NMR shifts of vinylic peaks listed in red.

The determination of the stereoselectivity in this reaction was complicated by the observation that the initial products **2** and **3** are susceptible to a further reaction affording the disubstituted product **4** as can be seen in Figure 3-1. To determine the kinetic selectivity between **2** and **3** as well as the relative rates of their formation versus their conversion to **4**, the product mixture versus conversion was determined then modeled kinetically. The relative amounts of **1**:**4** in the product mixture were obtained at a series of conversions using limiting amounts of the sodium para-tolylthiolate, followed by ¹H-NMR analysis of worked-up aliquots by comparing the integrations of the vinylic peak for each compound, located at δ 6.12, 6.32, 5.96, and 5.78 for **1**, **2**, **3**, and **4**, respectively. The vinylic peaks representing each of the four compounds were assigned by using NMR correlation calculations which predicted a chemical shift of 6.34 ppm for **2** and

5.98 ppm for **3**. The kinetic modeling of the product mixture assumed that all of the conversions were bimolecular, and the relative values of the rate constants were adjusted to optimally match the observed compositions. The resulting relative rates were 4.5, 1, 3.3, 3.7 for k_1 , k_2 , k_3 , and k_4 , respectively. As can be deduced from the relative rates, the experimental product ratio of **2:3** was found to be 4.5:1.

The preference for formation of **2** over **3** was expected from the previous observations of Barton for reactions of **1** with lithium dimethylcuprate.³² This was further supported in studies by Dieter et al. which utilized a combination of UV Spectroscopy, NMR and X-ray crystallography to show definitively that the major product in these substitutions was the product formed by the stereospecific addition of the nucleophile in a syn fashion to the activating group.³³

Theoretical Studies

From a theoretical perspective, the interesting aspect of the experimental observations is that **3** is formed at all; as will be discussed; conventional computational studies do not rationalize its formation. A series of computational levels were employed to locate the transition structure/s associated with the nucleophilic substitution of **1** by sodium para-tolylthiolate.

In B3LYP/6-31+G** calculations employing a PCM solvent model for ethanol, transition structure **5** was located, leading (by IRC) to the formation of **2**. Three notable features were common to all of the calculational results. The first is that no intermediates could be located. While there is some question whether a PCM solvent model would be satisfactory for locating intermediates in reactions of this type, by taking the relatively high nucleofugality of chloride substituents into account, then the concerted process would fit with the general expectations of these reactions as outlined by Guthrie. The second feature is that at transition structure **5**, no clear structural decision has been made regarding which chloride will be displaced. This is apparent as the bond lengths of both C-Cl bonds at the TS are almost identical (differ by less than 0.01 Å). The third and most striking feature is that only transition structures leading to **2** were locatable. Despite extensive effort, no substitution transition structure leading by IRC to **3** could be located in any calculation. However, it can be expected that products **2** and **3** can interconvert via the rotational transition state, **6**.

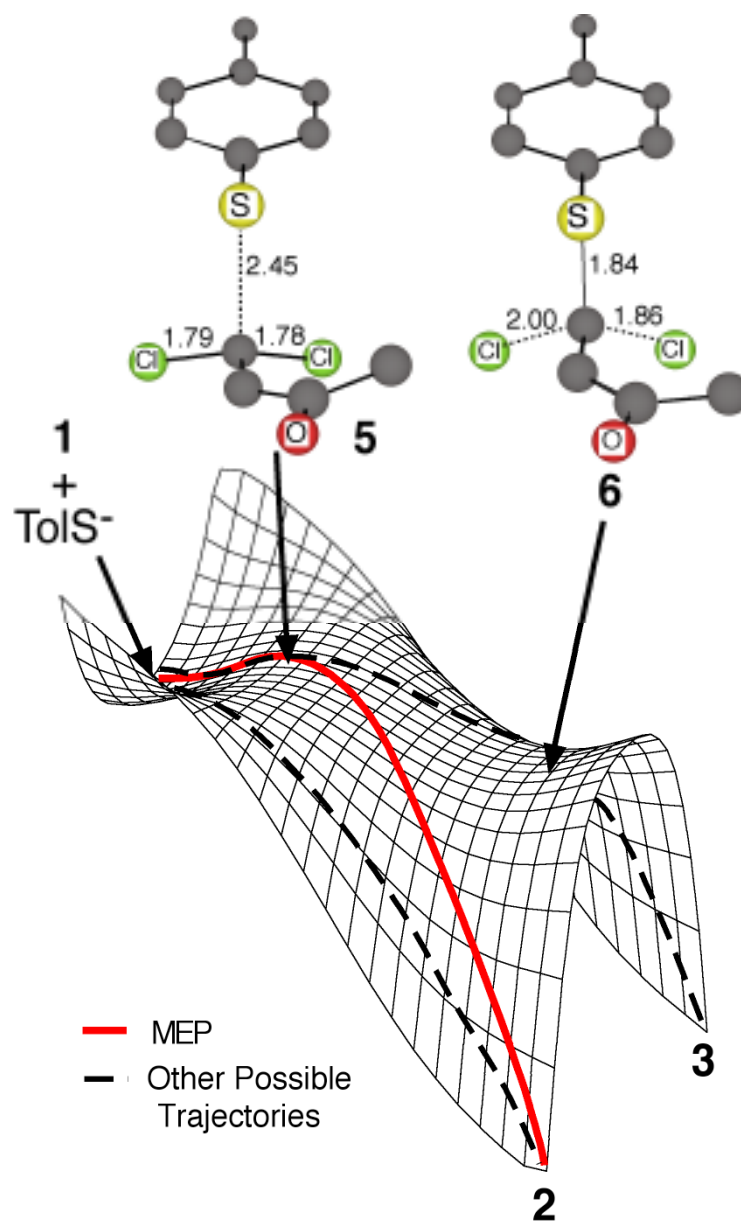


Figure 3-2. Qualitative Energy Surface for the Nucleophilic Substitution of **1**.

Discussion

The phenomenon of a single transition structure leading to two different products is representative of reactions involving a bifurcation in the potential energy surface (PES) and consequently, representative of a system where the selectivity is controlled by dynamic effects.³⁴ In such systems, one would expect the PES to resemble that depicted in Figure 3-2. Trajectories on this surface could first pass through an addition transition state and give either product **2** or **3**, effectively bypassing both the tetrahedral intermediate and the subsequent elimination transition state. Under these circumstances, the “structural decision” is made beyond **5** and determines which chloride is displaced and ultimately, which product is formed.

As stated earlier, adherence to conventional transition state theory would require the existence of two competing transition structures leading to either product. Our ability to locate only a single transition structure, from which both products can be obtained via direct/indirect routes, is characteristic of systems where the observed selectivity is being determined by dynamic effects. Furthermore, if this hypothesis is indeed true, then we would expect our trajectory calculations to arrive at results that are consistent with the experimentally determined product ratio.

Quasiclassical direct-dynamics trajectories on a PCM B3LYP/6-31+G** energy surface were initiated from PCM transition state, **5**. Each normal mode of the TS was given its zero point energy plus a Boltzmann sampling of additional energy appropriate for 298.15 K, with a random phase and sign for its initial velocity. The mode associated with the imaginary frequency was given a Boltzmann sampling of energy “forward”

over the col. A Verlet algorithm was employed to propagate the trajectories and 1-fs steps were taken until product formation was observed. The median time for formation of products **2** and **3** was found to be 85 and 94 fs respectively. The numbers of trajectories resulting in the formation of either product **2** or **3** were counted to give a predicted product ratio of 2.4:1.

As hypothesized, the trajectory studies predict a ratio that is in direct agreement with that observed experimentally. Initially, a 2.4:1 predicted ratio may seem significantly different from the 4.5:1 ratio observed experimentally but upon closer examination it becomes apparent that this is most certainly not the case. If the corresponding amount of each product represented by the given ratios is determined, then 2.4:1 represents a 70:30 ratio and 4.5:1 represents an 81:19 ratio of products **2** and **3** respectively. In addition, trajectory results also show a clear preference for the addition of the thiolate nucleophile in a syn fashion to the ketone substituent and are consistent with previous results obtained for similar substitutions on analogous systems.³⁵

In summary, the inability to locate any intermediates on the potential energy surface confirms that the substitution is concerted and could potentially be governed by dynamic effects. Computational studies employing a PCM solvent model, located only a single transition state, leading directly to the major product. This is inconsistent with conventional TST and as per the rules of TST, we would expect to locate two separate competing transition states leading to either product. Finally, the remarkable agreement between the experimental product ratios and the ratios predicted by dynamic trajectory

studies provides further evidence that the mechanism of substitution is concerted and the stereoselectivity is controlled by dynamic effects.

Experimental Section

General

Oven-dried glassware was cooled under a stream of nitrogen prior to use and the reaction was run under positive N₂ pressure. All chemicals used were obtained commercially and 4.5 Å molecular sieves were added to solvents to maintain dryness when necessary. The reaction apparatus for the synthesis of the dichlorobutenone was a 500 mL three-necked round bottom flask equipped with an addition funnel and a nitrogen line. The system was purged with N₂ prior to use. The distillation apparatus was a 500 mL round-bottomed flask connected to a Vigreux column and a short-path distillation head. A 6 torr oil-free vacuum pump was used as the vacuum source.

Synthesis of 4,4-dichloro-3-buten-2-one³¹. To 100 mL of dry CH₂Cl₂ was added 14.0g (0.11 moles) of anhydrous AlCl₃ and the mixture was allowed to stir in an ice bath for 15 minutes. To this slurry was added 8.0 mL (8.8g, 0.11 moles) of acetyl chloride dissolved in 20 mL of CH₂Cl₂ via addition funnel over 15 minutes. After the addition, the solution was allowed to warm up to room temperature and stir for about 5 hrs, allowing adequate time for the formation of the acetyl chloride-AlCl₃ complex. Subsequently, 8.0 mL (9.70g, 0.10moles) of vinylidene chloride dissolved in 20 mL CH₂Cl₂ of was then added slowly over 30 minutes. The reaction mixture was quenched after approximately

20 hrs by stirring in crushed ice for 15 mins and then it was filtered. This ensured that any excess acetyl chloride was hydrolyzed and also got rid of any emulsions that would affect separation of the phases. It was then extracted with 3 x 200 mL portions of CH_2Cl_2 after which the organic layers were combined. The combined organic layers were then washed with 3 x 200 mL of water and then stirred and cooled while 30 mL (21.9g, 0.22 moles) of Et_3N was added slowly over 30 mins. The reaction was allowed to run for 10 hrs and then quenched with 300 mL of 10% HCl solution. The organic layer was washed with 2 x 100 mL of 10% HCl solution and then dried with CaSO_4 and filtered. The dried reaction mixture was first concentrated by distilling off the CH_2Cl_2 under atmospheric pressure and then the desired dichloroenone product distilled under reduced pressure using a short Vigreux column at $\sim 40^\circ\text{C}/6$ Torr.

Reaction Kinetics of 4,4-dichloro-3-buten-2-one with Sodium-paratolylthiolate. Kinetic studies were carried out by dissolving 0.7g (5 mmol) of the dichloroenone into 30 mL of anhydrous ethanol in a 100 mL round bottomed flask. While being stirred under N_2 , 0.22g (1.5 mmol or 0.3 equivalents) of sodium-paratolylthiolate was added and allowed to react for 1h. An aliquot (0.7 mL) was then taken, washed with a 1:1 $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$ solution, dried and analyzed by $^1\text{H-NMR}$ to determine the relative amounts of each product as well as unreacted starting material. Immediately after taking an aliquot, an additional 0.1 equivalents (0.5 mmol) of the thiolate was added and allowed to react for 30 mins until the next aliquot was taken. This was repeated until the reaction was close to completion i.e. all the dichloroenone had

reacted. It was deemed important to keep the concentration of the thiolate nucleophile low to minimize the inevitable formation of the disubstituted byproduct. The relative amounts of each product for given equivalents of thiolate are listed in Tables 3-1 and 3-2.

Table 3-1. First kinetic study of the reaction of the thiolate with **1**.

Thiolate (equiv.)	Major product (%)	Dichloroenone (%)	Minor product (%)	Disubstituted Product (%)
0	-	100	-	-
0.3	8.6	83.9	2.8	4.7
0.4	16.0	76.8	4.6	2.7
0.5	20.2	65.8	6.8	7.2
0.6	25.2	60.9	6.3	7.6
0.7	30.2	49.5	8.8	11.5
1.0	45.8	16.5	15.9	21.8
1.1	49.9	9.0	15.8	25.4
1.2	51.8	5.2	14.9	28.1

Table 3-2. Second kinetic study of the reaction of the thiolate with **1**.

Thiolate (equiv.)	Major product (%)	Dichloroenone (%)	Minor product (%)	Disubstituted Product (%)
0	-	100	-	-
0.8	29.0	43.1	11.1	16.8
0.9	32.9	39.4	10.9	16.9
1.0	37.8	29.6	8.5	24.2
1.1	42.3	22.9	8.6	26.3
1.2	44.1	17.8	11.1	27.1
1.3	42.5	12.3	13.9	31.3
1.4	35.2	6.3	16.8	41.7

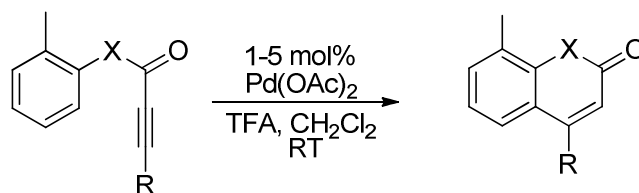
CHAPTER IV

MECHANISM OF THE FUJIWARA HYDROARYLATION

Introduction

It has long been realized that the activation of C-H bonds, which are ubiquitous in nature, would present a wide range of synthetic possibilities. Even more so, selective C-H activation would undoubtedly provide chemists with a powerful synthetic tool. Consequently, significant effort has been put into the development of methodology towards achieving this goal.^{36,37,38}

Over the past two decades, significant advances have been made in the use of transition metal catalysts in C-C bond formation processes.³⁹ In 2000, Fujiwara and coworkers reported the catalytic intramolecular hydroarylation of alkenes and alkynes using both palladium and platinum acetate in trifluoroacetic acid to synthesize a variety of coumarins and quinolinones (Fig. 4-1).⁴⁰ Coumarins and quinolinones have stimulated a substantial amount of interest because of their numerous applications as therapeutic agents.⁴¹



For coumarins X=O, for quinolinones X=NH
R represents a variety of alkyl or aryl groups

Figure 4-1. Synthesis of Coumarins and Quinolinones.

Initially, Fujiwara and coworkers proposed that the ring closure occurred via a “C-H activation” mechanism, see Figure 4-1.^{42a} This proposed C-H activation mechanism was defined by a series of transformations. Firstly, the Pd(II) species coordinates to the alkyne, the C-H bond is then activated to form the aryl-palladium complex **II**, trans insertion of the alkyne into the Pd-Aryl bond forms **III** and finally, protonation of **III** forms the coumarin product. However, this proposed mechanism was based on experimental results that provided support for the involvement of TFA in the protonolysis step but did not provide any evidence regarding the formation of the palladacycle **II**.

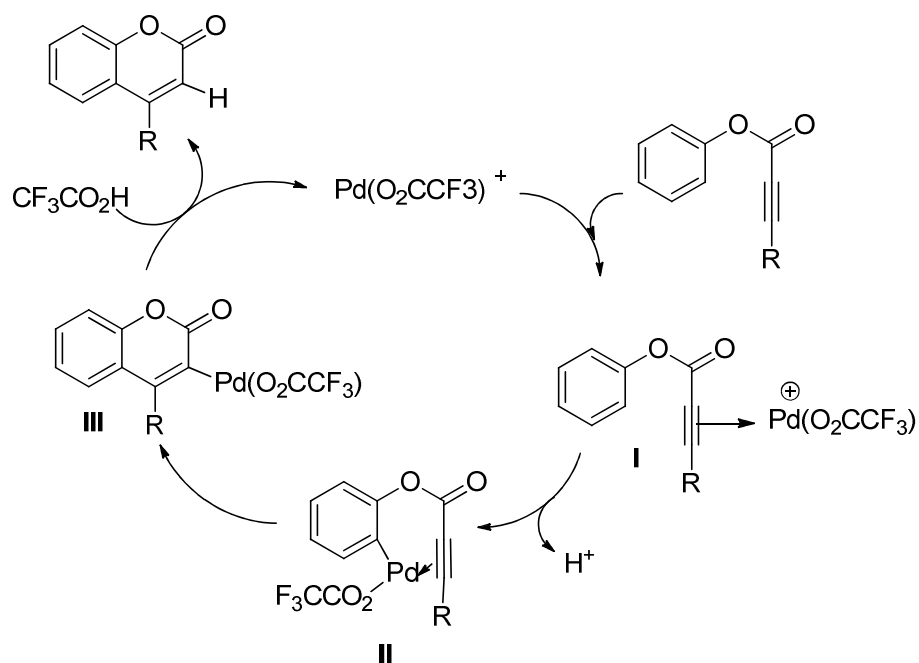


Figure 4-2. Hydroarylation by “C-H activation.”

In 2005, Tunge and coworkers⁴³ proposed a second mechanism for the hydroarylation reaction involving an electrophilic aromatic substitution process. As depicted in Figure 4-3, it is apparent that the EAS mechanistic cycle is strikingly similar to that of the “C-H activation” mechanism, the characteristic difference being that **I** is converted to **III** via a Wheland intermediate **IV**.

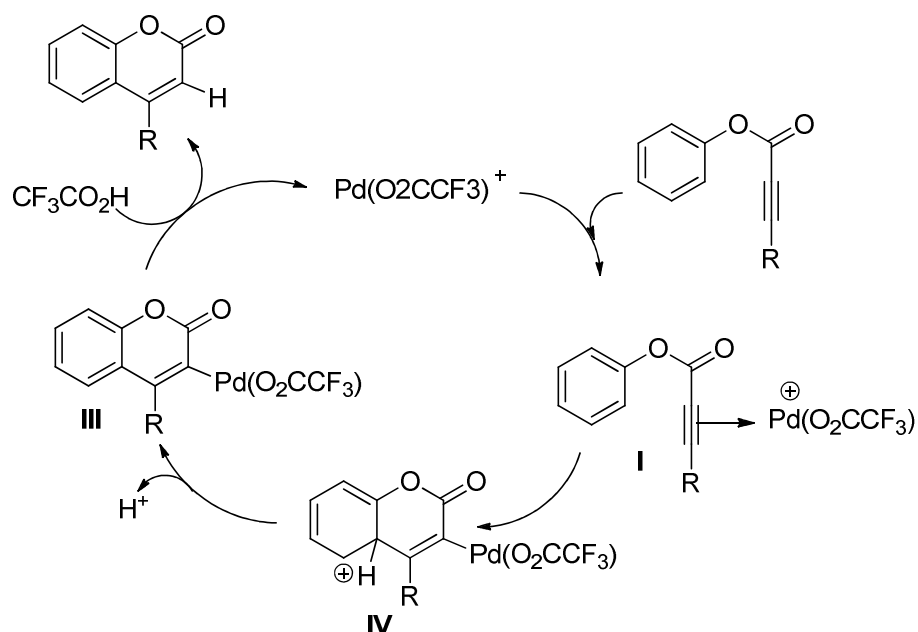


Figure 4-3. Hydroarylation by EAS.

Ultimately, this chapter will show that the determination of intermolecular kinetic isotope effects using natural abundance NMR methodology combined with theoretical calculations is highly suitable for deducing which of the two proposed mechanisms best describes the hydroarylation.

Results

The Pd-catalyzed ring closure of ortho-tolyl 3-phenylpropiolate **1**, to give the ring-closed 4-phenyl-8-methyl coumarin **2** was chosen for analysis, see Figure 4-4. This substrate was chosen particularly because it ensures that the C-C bond formation occurs on only one position of the aryl ring. In other words, only a single cyclized product will be formed in the reaction mixture.

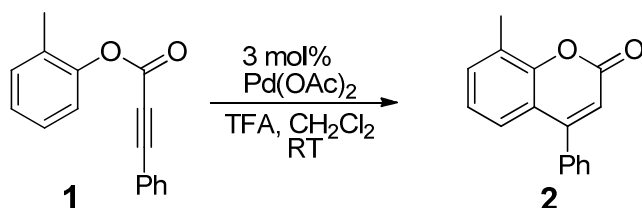


Figure 4-4. KIE Reaction Taken To ~ 80% Conversion.

It should also be noted that several control reactions were performed to ensure that the Pd catalyst was indeed necessary for the hydroarylation. Firstly, **1** was subjected to reaction conditions in the absence of the Pd catalyst and the reaction mixture was allowed to stir for 13hrs. The reaction was quenched, worked up and analyzed using H-NMR spectroscopy to confirm the absence of **2**. A second control reaction was ran with the catalyst being replaced by a strong Lewis acid, AlCl₃ and again, no **2** was observed by H-NMR spectroscopy. The results from both control reactions confirmed that the Pd catalyst was indeed necessary for coumarin formation.

Intermolecular ¹³C KIEs

The intermolecular ¹³C KIEs for the hydroarylation of **1** were determined at natural abundance using the Singleton NMR methodology. Two reactions catalyzed by 3 mole percent Pd(OAc)₂ in dry CH₂Cl₂ at 25 °C were taken to 85 ± 2 % conversion and 85 ± 2 % conversion (determined by ¹H-NMR), quenched, and unreacted starting material was recovered following an aqueous workup, concentration under reduced pressure and column chromatography. In each case, the ¹³C composition at each position

in the recovered samples was determined using the Singleton ^{13}C -NMR methodology and compared to ^{13}C composition of standard samples that were never subjected to reaction conditions. The relative ^{13}C compositions were determined by using the ortho carbons of the phenyl group as an internal standard, with the assumption that their individual isotopic compositions remained constant throughout the reaction. The intermolecular KIEs so determined are listed in Figure 4-5.

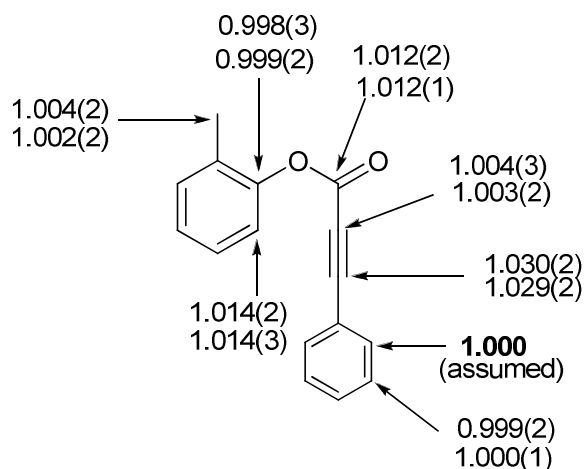


Figure 4-5. Intermolecular ^{13}C KIEs ($k^{12}\text{C}/k^{13}\text{C}$). Palladium catalyzed Fujiwara Hydroarylation of ortho-tolyl 3-phenylpropiolate **1** to give 4-phenyl 8-methyl coumarin **2**. Both sets of KIEs represent two independent experiments and the standard deviations of these measurements are indicated in parentheses. Experimental KIEs at all other unlabeled positions are unity.

The main observation here is that the isotope effects for the bonding carbons, aryl carbon α to the ester and alkynyl carbon α to phenyl are both large. Qualitatively,

this implies that the C-C bond formation is occurring in the rate limiting step. Curiously, both sets of data display a significant isotope effect at the carbonyl group which is very surprising and up to this point an explanation for its origin has been elusive.

Theoretical Studies

Modeling transition-metal catalyzed processes computationally can be quite challenging depending on the complexity of the system being studied. As a result, there are numerous methods available which are suitable depending on the nature of the system. Consequently, this study was undertaken bearing in mind that a broad spectrum of methods would be needed. Both gas phase and various solvent models were utilized to locate the transition structure via which **1** is converted into **2**. Best agreement between experimentally determined KIEs and theoretical predictions was achieved when a gas phase B3LYP/6-31G* method was used for C, H, O and F and LANL2DZ for Pd.

The ^{13}C KIEs based on **TS1** were predicted from scaled theoretical vibrational frequencies using conventional transition state theory by the Bigeleisen and Mayer method and are listed in Figure 4-6. It should also be noted that KIE predictions based on the various transition states located, all showed a significant isotope effect at the carbonyl C, an observation which is also present in experimental KIEs.

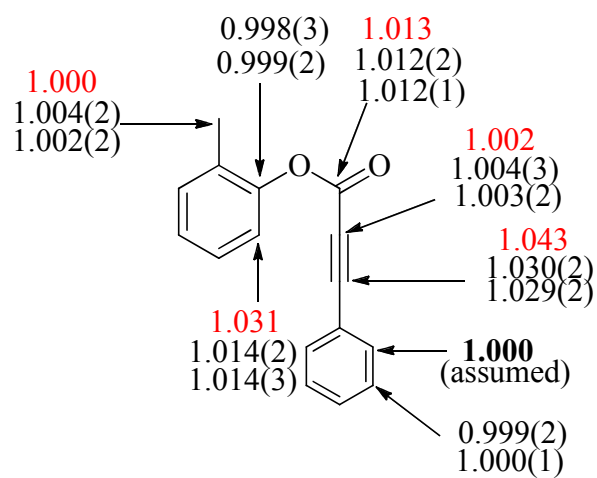
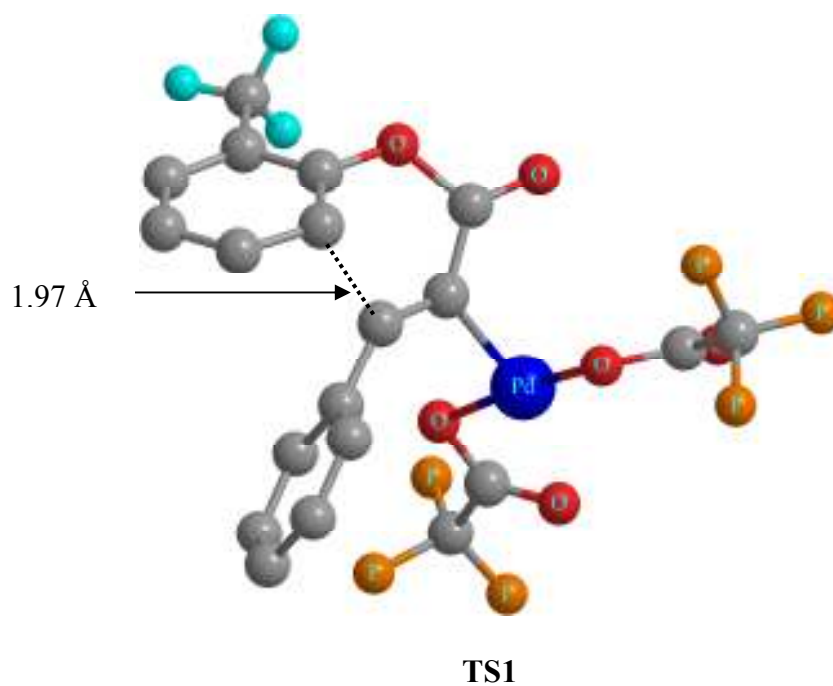


Figure 4-6. Predicted KIEs (red) calculated from **TS1**. Experimentally determined KIEs (black) are also listed.

Discussion

The C-H activation mechanism proposed by Fujiwara is particularly intriguing since it invokes an unusual trans-addition of the Pd-Ar bond across the alkyne. While there are a handful of examples of these unusual trans-additions to alkynes, aryl-palladium complexes have shown a strong preference for cis-addition to alkynes.⁴⁴ As a result, the overall stereochemistry observed for the hydroarylation aligns well with the proposed EAS mechanism as electrophilic attack of alkynes towards nucleophilic attack commonly occurs via a trans-addition.⁴⁵ The intermolecular ¹³C KIEs determined experimentally, also support the proposed EAS mechanism and large isotope effects on the acetylene carbon and aryl carbons are symbolic of rate limiting C-C bond formation.

Experimental Section

General

Oven-dried glassware was cooled under a stream of nitrogen prior to use and the reaction was run under positive N₂ pressure. All chemicals used were obtained commercially and 4.5 Å molecular sieves were added to solvents to maintain dryness when necessary. The reaction vessels were purged with N₂ prior to use.

Phenyl Propiolyl Chloride. Example Procedure. To 200 mL of dry chloroform, 25.0g (0.17 moles) of phenyl propiolic acid was dissolved with stirring. This was followed by the addition of 50 mL (0.68 moles) of thionyl chloride and the mixture was

allowed to react for 3-5 hrs under reflux. Excess thionyl chloride was then removed via vacuum distillation to give the concentrated acid chloride.

O-tolyl 3-phenyl Propiolate. Example Procedure. The recovered acid chloride was dissolved in 200mL of chloroform and ~1.5 equivalents (23 mmoles) of ortho-cresol were then added. This mixture was then allowed to react under reflux and the overall conversion was monitored using NMR. Whenever the relative amount of o-cresol stabilized, the heat source was removed and then the mixture was concentrated under reduced pressure to give a yellow solid. This yellow solid was purified by recrystallizing from hexanes. The white crystals so formed were then rinsed with a cold solution of hexanes and allowed to dry.

Palladium Catalyzed Ring Closure. Example Procedure. Under positive N₂ pressure, 7.05 g (28 mmoles) of **1** was dissolved in a mixture of 14 mL dichloromethane and 42 mL trifluoroacetic acid with stirring. To this solution, 188 mg (0.83 mmoles) of Pd(OAc)₂ was then added and allowed to react at room temperature for 4 h. The overall percent conversion was determined using H-NMR by monitoring the vinylic proton of the coumarin product. The reaction was then quenched with brine and extracted into ether when the conversion approached 80%. The organic layer was washed with brine and then with 10% sodium carbonate until fizzing ceased. The diethyl ether was distilled under reduced pressure and the remaining starting material was isolated by flash column chromatography using a 2:3 dichloromethane:hexanes solution as eluent. Two identical

reactions were run and taken to 84.8 % and 84.9 % conversion. The remaining starting material was isolated from each reaction and analyzed by ^{13}C -NMR spectroscopy using CDCl_3 as a solvent.

CHAPTER V

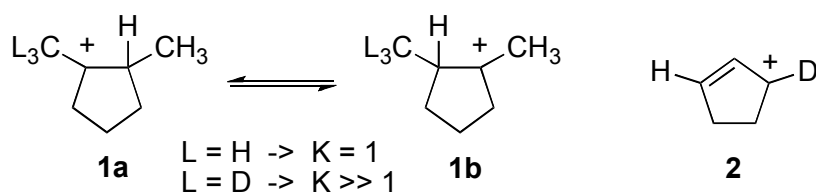
**DISTINGUISHING BETWEEN ISOTOPIC PERTURBATION OF EQUILIBRIA
AND ISOTOPE-INDUCED DESYMMETRIZATION**

Introduction

It is well understood that isotopic substitution desymmetrizes the time-averaged geometry of otherwise symmetrical structures.⁴⁶ However, the effect of isotopic substitution on geometry is often assumed to be small, and this assumption is central to a number of experimental observations. We describe here a way in which the effect of isotopic substitution on the geometry of a symmetrical structure can be surprisingly large and how this can mislead the interpretation of experimental observations.

The experimental distinction between a symmetrical structure versus two degenerate equilibrating structures of lower symmetry has been a common problem in chemistry. This issue is most vexing when the conjectured equilibration would be rapid and the applicable spectroscopic techniques have a low time resolution, as in NMR studies of simple molecules. To address this problem, Saunders developed one of the most elegant experiments of classical physical organic chemistry in the observation of isotopic perturbation effects on the NMR spectra of molecules of interest.⁴⁷ The Saunders experiment proved its power by convincingly addressing the structure of the norbornyl cation,⁴⁸ and over the last 30 years it has been employed broadly in organic and organometallic chemistry.^{49, 50, 51}

The idea behind the Saunders experiment is that desymmetrizing isotopic substitution affects the equilibrium between two equilibrating structures but cannot have a strictly analogous effect on a single symmetrical structure where no equilibration is present. For example, deuterium substitution in a methyl group of **1a/1b** strongly affects the equilibrium between structures that would otherwise be degenerate. The ^{13}C NMR spectrum of **1** with $L = \text{D}$ reflects the breaking of the degeneracy, and widely separate signals are observed for carbons that were overlapping in the unlabeled **1** ($L = \text{H}$). With **2**, in contrast, there is no equilibrium to affect. The NMR spectrum of **2** still reflects an asymmetry that results from intrinsic isotope effects on chemical shifts, but the separation of carbons that were equivalent in the unlabeled structure is much smaller than in the case of **1**. As a result, the ^{13}C NMR spectra of **1** ($L = \text{D}$) versus **2** readily distinguish the equilibrating from non-equilibrating structures.



We envisioned that under certain circumstances the intrinsic isotope effects on the chemical shifts for single "symmetrical" structures might be much larger than normally anticipated, making these structures appear to be unsymmetrical equilibrating structures. Intrinsic isotope effects on chemical shifts can occur in purely harmonic

systems, but the largest effects should in general be associated with changes in the time-averaged geometry of a molecule upon isotopic substitution. This requires anharmonicity. Changes in molecular geometry, such as differing C-H and C-D bond lengths, can arise from simple cubic terms in the potential V versus normal coordinate displacement Q without any coupling of normal modes, e.g., from α_{iii} terms in Figure 5-1 with all $\alpha_{ijj} = 0$. However, the resulting isotope effects on the shift of atoms more than one bond distant are generally small. The more interesting effect of anharmonicity that we considered would arise when a mode i (or a series of modes), whose zero-point energy (zpe) is affected strongly by isotopic substitution, is coupled ($|\alpha_{ijj}| \gg 0$) with a mode j that desymmetrizes an otherwise symmetrical molecule. In such a case, isotopic substitution in i can affect the time-averaged displacement of the "distant" mode j .

$$V = \sum_i k_{ii} Q_i^2 + \sum_i \alpha_{iii} Q_i^3 + \sum_{i,j(i \neq j)} \alpha_{ijj} Q_i^2 Q_j + \mathcal{L}$$

Figure 5-1. Anharmonic Potential with Respect to Coordinate Displacement.

An example of this phenomenon arises in the bromonium ion derived from tetramethylethylene (**3**). Ohta and coworkers found that the ^{13}C NMR signals for the quaternary carbons in **3** are separated ("D") by 3.61 ppm.⁵⁰ This shift is more than an order of magnitude larger than normal two-bond intrinsic H/D isotope effect on a ^{13}C chemical shift in the absence of equilibrating structures. Accordingly, Ohta concluded

that **3** is not a 1,2-bridged structure (**3a**), but rather is a rapid equilibrium of b-bromocarbenium ions (**3b**). The data appeared to force this conclusion, but it is a bothersome one since a long history of experimental observations has supported the bridged structure, as reflected in every undergraduate textbook of organic chemistry. In addition, theoretically calculated potential-energy minima for **3** uniformly have the C_{2v} symmetry of the bridged ion **3a**.

Results

In the calculated C_{2v} structures for **3a**, such as the MPW1PW91/6-31+G**⁵² structure **4** in Figure 5-2, a low-energy B_2 mode " j " ($133X\text{ cm}^{-1}$) rocks the axis of the central C-C bond versus the bromine atom. If motion of the bromine atom toward the CH_3 groups is defined as "positive" motion in j , then a series of modes associated with C-H stretching and bending vibrations exhibit positive cubic force constants a_{ij} (i being the stretching and bending modes), while an equivalent series of modes associated with C-D stretching and bending vibrations exhibit negative a_{ij} (calculated from finite differences of Cartesian Hessians⁵³). In other words, motion of the bromine atom toward the CH_3 groups strengthens the C-H stretching and bending vibrations, particularly those associated with the hydrogens anti to the bromine atom, while weakening the corresponding C-D vibrations. This fits with the intuitive structural ideas used to understand b-deuterium isotope effects in carbocations. Because of the lower zero-point energy in C-D vibrations, the molecular zero-point energy is decreased as the bromine is displaced toward the CD_3 groups. Based on the cubic force constants, the difference in

zero-point energy between the two classical turning points of mode j would be about 20 cm^{-1} . This is a substantial correction relative to the potential energy curve for mode j and should lead to a significant time-averaged displacement of mode j away from the C_{2v} structure.

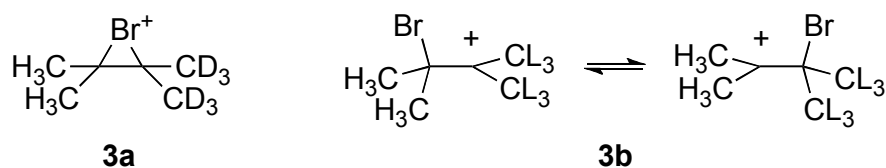


Figure 5-2. Bromonium Cation (3a) and Equilibrating Bromocarbenium Species (3b).

We used three methods to estimate the desymmetrization of **3** and the effect of this desymmetrization on its NMR spectra. The first and conceptually simplest approach treats the motion in the low-energy mode j as slow and separable from the motion in the other modes, so that the zero-point energy in the other modes can be applied directly as a correction to the energy curve governing mode j . Numerical solution of Schrodinger's equation for the resulting energy curve affords a wavefunction from which the average displacement of mode j can be calculated. The overall structure **5a** from this "one-dimensional" approach then assumes that all other modes are at their potential energy minimum. The second method applied second-order perturbation theory based on the cubic and semi-diagonal quartic force constants,⁵⁴ resulting in structure **5b**. The third method made use of quasiclassical direct-dynamics trajectory calculations. A series of quasiclassical trajectories on the MPW1PW91/6-31+G** surface were started from **4**

giving each normal mode its ZPE plus a Boltzmann sampling of additional energy appropriate for the temperature of the simulation. Using a Verlet algorithm, trajectories were continued to a time limit of 500 fs.⁵⁵ The trajectory geometries (>100,000 in each case) in curvilinear coordinates were then averaged, affording structures **5c**, **5d**, and **5e** at 0, 193, or 298 K, respectively.

All three methods predict significant desymmetrization of the bromonium ion. For comparison, the change in the C-Br bond length in (CH₃)₂CHBr versus (CD₃)₂CHBr as predicted by the second-order perturbation theory method is only 0.0004 Å, so the geometry change in **5** is a factor of 20 greater than might have been expected from a structurally similar model. The trajectory method predicts somewhat greater desymmetrization than either the one-dimensional or perturbation theory approach. A notable observation is that the desymmetrization increases with temperature.

It is overly simplistic but enlightening to calculate the NMR spectra based on these time-averaged structures. For each geometry **5a-e**, the separation of the quarternary carbon ¹³C chemical shifts, Δ, was calculated by the GIAO method (mPWPW91/6-31+G**), and the results are summarized in Figure 5-3. The striking observation is that the predicted Δ for each structure is in the range of the experimentally observed Δ. In other words, the experimental observation appears to result from the large change in the time-averaged geometry of the molecule due to the anharmonicity effect describes above. However, these single structure calculations do not allow for the change in the span of accessed nuclear configurations due to isotopic substitution. We therefore employed the non-simplistic, if arduous, approach of calculating Δ based on NMR

calculations at each point of the trajectories at 193 K. The result is again in the range of the experimentally observed Δ . Overall, as is consistent with both classical mechanistic studies and computational studies, the NMR observation may be explained without the need to postulate any asymmetry in the unlabeled bromonium ion.

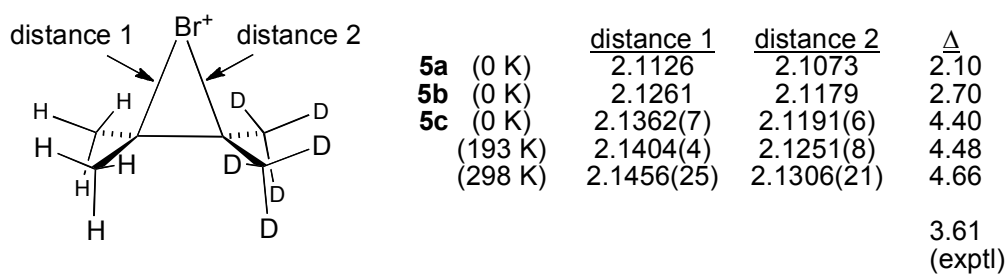
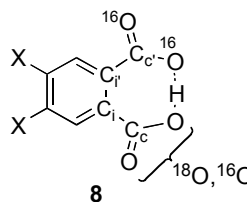
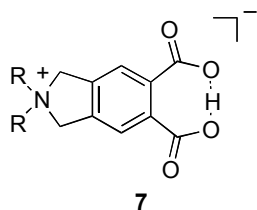
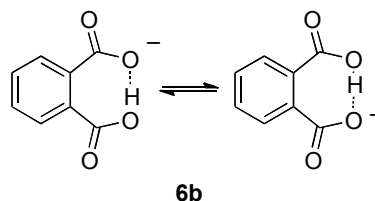
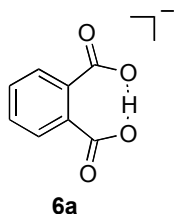


Figure 5-3. Intrinsic Chemical Shifts.

A difficult but more broadly important example to consider is the hydrogen phthalate anion **6**. The nature of the hydrogen bond (H-bond) in anions of this type has been of considerable interest, both from fundamental perspective and with regard to the disputed importance of "low-barrier" or "short, strong" H-bonds in catalysis. The structure of **6** has been considered in terms of two limiting possibilities, either having the proton centered between the oxygens as in the "symmetrical" **6a**, or having the proton localized in one well of a double-well potential with a rapid equilibration of the two tautomeric forms as in the "asymmetric" **6b**. X-ray and neutron diffraction studies have observed the symmetrical structure, and gas-phase computational studies have also favored this structure. The interesting question has been the structure of the anion in solution. Primary isotope effects on the chemical shift in **6**, i.e. comparison of the

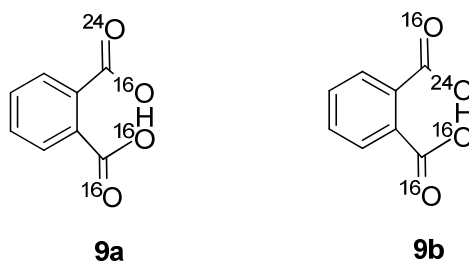
chemical shifts of H versus D versus T have favored the symmetrical structure in solution.⁵⁶ However, a series of papers by Perrin and coworkers have applied a Saunders-type isotopic perturbation experiment to **6** and a variety of related ions, and in all cases the experimental observations have been interpreted as supporting asymmetric structures.⁴⁹ Perhaps the most striking observation is that the isotopic perturbation experiment appears to support an asymmetric structure for **7**, a molecule designed to avoid desymmetrizing counterion effects, even in relatively non-polar methylene chloride solutions. The sweeping conclusion from these observations has been that "H-bonds are not symmetric in solution".^{49c} Rather, the necessarily asymmetric instantaneous environment effected by any solvent is taken as sufficient to break the molecular symmetry. By extension, these studies have been interpreted as denying any extra stabilization associated with short-strong hydrogen bonds.⁵⁵



The key Perrin experiment involves the study of hydrogen phthalates containing a single ^{18}O -label, as in **8**. The presence of the ^{18}O leads to a separation of the ^{13}C NMR signals (Δ_{obs}) for carboxylate carbons C_c versus C_c' and ipso carbons C_i versus C_i' . Assuming that the peak separation in the corresponding diacid forms under identical conditions represents the intrinsic isotope effects on the chemical shift, Δ_0 , the consistent observation that $|\Delta_{\text{obs}}| > |\Delta_0|$ triggers the conclusion that that hydrogen phthalate ions consist of equilibrating tautomers rather than single symmetrical structures. However, outside of water and methanol, the carboxylate carbons were not diagnostic of equilibrating tautomers owing to very low differences between Δ_{obs} and Δ_0 , ≤ 4 ppb. Instead, conclusions relied on observations of Δ_{obs} versus Δ_0 for the ipso carbons. For **7** (R = octyl) in CD_2Cl_2 , $-\Delta_{\text{obs}}$ was 12 ppb while $-\Delta_0$ was only 2 ppb, and this difference was considered to be conclusive support for equilibrating tautomers.

To explore whether the Δ_{obs} for the ipso carbons in hydrogen phthalates is consistent with the isotope-induced desymmetrization of a symmetrical structure, we applied the methods used to study **3**. All of the methods encounter substantial difficulties owing to the 200-fold smaller effect in phthalates versus **3**. All of the methods encounter substantial difficulties owing to the roughly 200-fold smaller effect of ^{18}O in phthalates versus deuterium in **3**, particularly with regard to numerical convergence. We ultimately focused on the most rigorous procedure of calculating the NMR spectrum at each point of a very large number of quasiclassical trajectories at 25 °C. This method itself has the substantial problem that the ^{18}O isotope effect on the chemical shifts in **8** converges exceedingly slowly relative to the small experimental Δ_{obs} . We estimate that it

would take an impractical 120,000,000 force and NMR calculations or 1500 processor years to obtain a satisfactory statistical significance for the predicted Δ_{obs} . To get around this problem, we employed the non-physical ^{24}O in trajectories making the assumption that this would increase the magnitude of the isotope effect by approximately a factor of 4. This decreases the computational cost by a factor of 16. A series of quasiclassical trajectories on the gas-phase MPW1PW91/6-31G* surface were initiated from **9a** and **9b** giving each normal mode its ZPE plus a Boltzmann sampling of additional energy appropriate for the 25 °C, along with a random phase and sign for its initial velocity. The trajectories were then propagated both forward and backward in time for 500 fs. At each point in the trajectories, the isotropic shielding was calculated by the GIAO method. The time-averaged Δ_0 was then calculated from the average of NMR shifts from approximately 5,000,000 trajectory points for **9a** and 2,500,000 trajectory points for **9b**.



As will be comforting to many organic chemists, the NMR observations are explained without the need to postulate any intrinsic asymmetry to a symmetrical bromonium ion. All three methods show strong agreement with the experimentally

determined chemical shifts of the bromonium ion. However, in the case of Hydrogen phthalate only the trajectory simulations give good predictions of the experimental result. Both the one-dimensional displacement method and the 2nd order perturbation theory methods are highly dependent on the desymmetrizing normal modes. In **3**, there is one major desymmetrizing mode and not much contribution from other modes. However, with regards to **9**, then one observes several different desymmetrizing modes all of which display significant hydrogen motion between both carboxylate O. The trajectory method, on the other hand, is unaffected by this wider distribution of asymmetry along several modes and consequently, no dropoff is observed in the predictions **3** to **9** are analysed.

CHAPTER VI

CONCLUSIONS

In the study of the ethanolysis of symmetric aryl carbonates, substrates with good leaving groups were found to have early transition states and are likely to undergo substitution in a concerted manner. Additionally, the unique structure of symmetric carbonates is such that upon nucleophilic attack at the carbonyl, one would expect an isotope effect to be generated in one of the atoms adjacent to the carbonyl. The presence of an ^{17}O isotope effect would be indicative of a concerted mechanism while its absence would mean the mechanism was stepwise. However, while we were unable to determine ^{17}O KIEs experimentally, it was shown conclusively using trajectory simulations that these reactions were in fact concerted and ultimately their selectivities would be determined by dynamic effects.

The reaction of 4,4-dichloro-3-buten-2-one with sodium para-tolylthiolate nucleophile, provided two distinguishable products and therefore, a measurable product ratio. We hypothesized that if our dynamic simulations predicted product ratios that showed good agreement with experimental results, then this would indicate that the selectivity was determined by dynamic effects. The predicted product ratio of 2.5:1 was in good agreement with the experimental ratio (4.5:1) and provides strong support for the mechanism being concerted and also for the stereoselectivity being controlled by dynamic effects.

Intermolecular ^{13}C KIEs are an efficient tool in deciding which of the two proposed mechanisms better describes the reaction. The large normal ^{13}C KIEs observed are indicative of rate limiting C-C bond formation and consequently, support the proposed EAS mechanism rather than a “C-H activation” mechanism..

The distinction between isotopic perturbation of equilibrium and isotope-induced desymmetrization with regards to the bromonium cation of tetramethylethylene and hydrogen phthalate was thoroughly explored. Prior to this work it was generally assumed that if the isotope effect of the chemical shift was large then automatically, this was thought to indicate the presence of two degenerate equilibrating structures. However, this study has been successful in showing that small changes in the time-averaged geometry of a single non-degenerate species can lead to a large isotope effect, hence creating the illusion of two equilibrating structures when that is not actually the case.

The application of TST to the observed selectivity in an organic reactions involves the assumption that each product is afforded by a different pathway and the relative amounts of each product is dependent on the relative energies of competing transition states. However, this work has shown that cases do exist where no competing transition states/pathway exists and instead these systems are defined by a bifurcation in the PES, on which the selectivity observed is under dynamic control. In other cases, it has been shown that the combination of KIEs, theoretical calculations and dynamic trajectory simulations is a powerful tool for the elucidation of reaction mechanisms.

REFERENCES

1. Singleton, D. A.; Thomas, J. B.; Waas, J. R.; Harmata, M. *J. Am. Chem. Soc.* **2008**, *130*, 14544-14555.
2. Singleton, D. A.; Thomas, A. A. *J. Am. Chem. Soc.* **1995**, *117*, 9357-9358.
3. Newman-Evans, R. H.; Carpenter, B. K. *J. Am. Chem. Soc.* **1984**, *106*, 7994-7995.
4. Carpenter, B. K. *Angew. Chem. Int. Ed.* **1998**, *37*, 3340-3350.
5. Vande Linde, S. R.; Hase, W. L. *J. Chem. Phys.* **1990**, *93*, 7962-7980.
6. Ussing, B. R.; Hang, C.; Singleton, D. A. *J. Am. Chem. Soc.* **2006**, *128*, 7594-7607.
7. (a) Metiu, H.; Ross, J.; Silbey, R.; George, T. F. *J. Chem. Phys.* **1974**, *61*, 3200-3209.
(b) Quapp, W.; Hirsch, M.; Heidrich, D. *Theor. Chem. Accounts* **1998**, *100*, 285-299.
(c) Valtazanos, P.; Ruedenberg, K. *Theor. Chim. Acta* **1986**, *69*, 281-307. (d) Quapp, W. *J. Mol. Struct.* **2004**, *695-696*, 95-101.
8. (a) Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1992**, *114*, 5879-5881. (b) Wenthold, P. G.; Hrovat, D. A.; Borden, W. T.; Lineberger, W. C. *Science* **1996**, *272*, 1456-1459.
9. Sun, L.; Song, K.; Hase, W. L., *Science* **2002**, *296*, 875-878.
10. Gonzalez-Lafont, A.; Moreno, M.; Lluch, J. M., *J. Am. Chem. Soc.* **2004**, *126*, 13089-13094.
11. (a) Bach, R. D.; Fox, J. M.; Dmitrenko, O.; Liao, L. *J. Org. Chem.* **2004**, *69*, 7317.
(b) Chrystiuk, E.; Williams, A. *J. Am. Chem. Soc.* **1987**, *109*, 3040. (c) Um, I. H.; Han, H. J.; Ahn, J. A.; Kang, S.; Buncl, E. *J. Org. Chem.* **2002**, *67*, 8475.

12. Bender, M. L. *J. Am. Chem. Soc.* **1951**, *73*, 1626-1629.
13. Bender, M. L.; Matsui, H.; Thomas, R. J.; Tobey, S. W. *J. Am. Chem. Soc.* **1961**, *83*, 4193-4196.
14. McClelland, R. A. *J. Am. Chem. Soc.* **1984**, *106*, 7579-7583.
15. (a) Ba-Saif, S.; Williams, A.; Luthra, A. K. *J. Am. Chem. Soc.* **1987**, *109*, 6362-6368.
(b) Ba-Saif, S.; Williams, A.; Luthra, A. K. *J. Am. Chem. Soc.* **1989**, *111*, 2647-2652.
16. Santos, J. G.; Castro, E. A.; Gazitúa, M. *J. Org. Chem.* **2005**, *70*, 8088-8092.
17. Castro, E. A.; Campodonico, P.; Toro, A.; Santos, J. G. *J. Org. Chem.* **2003**, *68*, 5930-5935.
18. Ault, A. *J. Chem. Educ.* **2007**, *84* (1), 38-39.
19. Singleton, D. A.; Thomas, A. A. *J. Am. Chem. Soc.* **1995**, *117*, 9357-9358.
20. Marlier, J. F.; O'Leary, M. H. *J. Am. Chem. Soc.* **1990**, *112*, 5996-5998.
21. (a) Bigeleisen, J.; Mayer, M. G. *J. Am. Chem. Soc.* **1947**, *15*, 261-267. (b) Wolfsberg, M. *Acc. Chem. Res.* **1972**, *5*, 225-233. (c) Bigeleisen, J. *J. Chem. Phys.* **1949**, *17*, 675-678.
22. Saunders, M.; Laidig, K. E.; Wolfsberg, M. *J. Am. Chem. Soc.* **1989**, *111*, 8989-8994.
23. Svensson, M.; Humbel, S.; Froese, R. D. J.; Matsubara, T.; Sieber, S.; Morokuma K. *J. Phys. Chem.* **1996**, *100*, 19357-19363.
24. Gresser, M. J.; Jencks, W. P. *J. Am. Chem. Soc.* **1977**, *99*, 6963-6970.
25. (a) Williams, A. *Acc. Chem. Res.* **1989**, *22*, 387-392. (b) Williams, A.; Curran, T. C.; Farrar, C. R.; Niazy, O. *J. Am. Chem. Soc.* **1980**, *102*, 6828-6837.

26. Castro, E. A.; Ramos, M.; Santos, J. G. *J. Org. Chem.* **2009**, *74*, 6374-6377.
27. Castro, E. A.; Soto, C.; Vasquez, B.; Santos, J. G. *ARKIVOC* **2008**, *10*, 151-160.
28. Castro, E. A.; Gazitua, M.; Santos, J. G. *J. Org. Chem.* **2005**, *70*, 8088-8092.
29. (a) Guthrie, J. P. *J. Am. Chem. Soc.* **1996**, *118*, 12878-12885. (b) Guthrie, J. P. *J. Am. Chem. Soc.* **1991**, *113*, 3941-3949.
30. Bach, R.; Baboul, A. G.; Schlegel, H. B. *J. Am. Chem. Soc.* **2001**, *123*, 5787-5793.
31. Wilson, B. D. *Synthesis*, **1992**, 283-284.
32. Barrett, A. G. M.; Morris, T. M.; Barton, D. H. R. *J. Chem. Soc., Perkin Trans. 1* **1980**, 2272-2277.
33. Dieter, R. K.; III, Silks, L. A.; Fishpugh, J. R.; Kastner, M. E. *J. Am. Chem. Soc.* **1985**, *107*, 4679-4692.
34. (a) Ussing, B. R.; Hang, C.; Singleton, D. A. *J. Am. Chem. Soc.* **2006**, *128*, 7594-7607. (b) Thomas, J. B.; Waas, J. R.; Harmata, M.; Singleton, D. A. *J. Am. Chem. Soc.* **2008**, *120*, 14544-14555.
35. (a) Rappoport, Z. *Acc. Chem. Res.* **1981**, *14*, 7-15. (b) Rappoport, Z. *J. Org. Chem.* **1982**, *47*, 1397-1408.
36. Green, M. L.; Knowles, P. J. *J. Chem. Soc. D.* **1970**, 1677-1677.
37. Foley, P.; Whitesides, G. M. *J. Am. Chem. Soc.* **1979**, *101*, 2732-2733.
38. (a) Hoyano, J. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1982**, *104*, 3723-3725. (b) Tsang, J. Y. K.; Buschhaus, M. S. A.; Legzdins, P. *J. Am. Chem. Soc.* **2007**, *129*, 5372-5373.

39. (a) Arndtsen, B. A.; Bergman, R. G.; Mobley, T. A.; Peterson, T. H. *Acc. Chem. Res.* **1995**, *28*, 154-162. (b) Jones, W. D. *Top. Organomet. Chem.* **1999**, *3*, 9-46. (c) Waltz, K. M.; Muhoro, C. N.; Hartwig, J. F. *Organometallics* **1999**, *18*, 3383-3393.
40. Jia, C.; Lu, W.; Oyamada, J.; Kitamura, T.; Matsuda, K.; Irie, M.; Fujiwara, Y. *J. Am. Chem. Soc.* **2000**, *122*, 7252-7263.
41. El-Nagdy, S.; Soliman, A. Y.; Bakeer, H. M.; Youssef, A. M. *J. Chem. Soc. Pakistan* **1990**, *12*, 230-234.
42. (a) Jia, C.; Piao, D.; Oyamada, J.; Lu, W.; Kitamura, T.; Fujiwara, Y. *Science* **2000**, *287*, 1992-1995. (b) Jia, C.; Piao, D.; Kitamura, T.; Fujiwara, Y. *J. Org. Chem.* **2000**, *65*, 7516-7522. (c) Jia, C.; Kitamura, T.; Fujiwara, Y. *Acc. Chem. Res.* **2001**, *34*, 633-639. (d) Viciu, M. S.; Stevens, E. D.; Petersen, J. L.; Nolan, S. P. *Organometallics* **2004**, *23*, 3752-3755.
43. Tunge, J. A.; Foresee, L. N. *Organometallics*, **2005**, *24*, 6440-6444.
44. Yagyu, T.; Hamada, M.; Osakada, K.; Yamamoto, T. *Organometallics* **2001**, *20*, 1087-1101
45. (a) Mendez, M.; Munoz, M. P.; Nevado, C.; Cardenas, D. J.; Echavarren, A. M. *J. Am. Chem. Soc.* **2001**, *123*, 10511-10520. (b) Fuerstner, A.; Stelzer, F.; Szillat, H. *J. Am. Chem. Soc.* **2001**, *123*, 11863-11869.
46. Laurie, V. W.; Herschbach, D. R. *J. Chem. Phys.* **1962**, *37*, 1687-1693.
47. (a) Saunders, M.; Telkowski, L.; Kates, M. R. *J. Am. Chem. Soc.* **1977**, *99*, 8070-8071. (b) Saunders, M.; Kates, M. R. *J. Am. Chem. Soc.* **1977**, *99*, 8071-8072. (c)

- Saunders, M.; Kates, M. R.; Wiberg, K. B.; Pratt, W. *J. Am. Chem. Soc.* **1977**, *99*, 8072-8073.
48. Saunders, M.; Kates, M. R. *J. Am. Chem. Soc.* **1980**, *102*, 6867-6868.
49. (a) Kirchen, R. P.; Ranganayakulu, K.; Sorensen, T. S. *J. Am. Chem. Soc.* **1987**, *109*, 7811-7816. (b) Oldham, W. J. Jr.; Hinkle, A. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1997**, *119*, 11028-11036. (c) Law, J. K.; Mellows, H.; Heinekey, D. M. *J. Am. Chem. Soc.* **2002**, *124*, 1024-1030. (d) Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1978**, *100*, 7726-7727. (e) Paneque, M.; Poveda, M. L.; Toboada, S.; *J. Am. Chem. Soc.* **1994**, *116*, 4519-4520. (f) Webster, C. E.; Singleton, D. A.; Scymanski, M. J.; Hall, M. B.; Zhao, C.; Jia, G.; Lin, Z. *J. Am. Chem. Soc.* **2001**, *123*, 9822-9829. (g) Kronja, O.; Kohli, T. -P.; Mayr, H.; Saunders, M. *J. Am. Chem. Soc.* **2000**, *122*, 8067-8070. (h) Kuno, L.; Biali, S. E. *J. Org. Chem.* **2009**, *74*, 48-57. (i) Verat, A. Y.; Pink, M. Fan, H.; Tomaszewski, J.; Caulton, K. G. *Organometallics* **2008**, *27*, 166-168. (j) Reich, H. J.; Sikorski, W. H.; Thompson, J. L.; Sanders, A. W.; Jones, A. C. *Org. Lett.* **2006**, *8*, 4003-4006. (k) Lawes, D. J.; Geftakis, S.; Ball, G. E. *J. Am. Chem. Soc.* **2005**, *127*, 4134-4135. (l) Tellers, D. M.; Bergman, R. G. *J. Am. Chem. Soc.* **2001**, *123*, 11508-11509.
50. (a) Ohta, B. K.; Hough, R. E.; Schubert, J. W. *Org. Lett.* **2007**, *9*, 2317-2320. (b) Earlier work had reached the opposite conclusion (Servis, K. L.; Domenick, R. L. **1985**, *107*, 7186-7187) but had been compromised by an unexpected isomerization as described.

51. (a) Perrin, C. L.; Thoburn, J. D. *J. Am. Chem. Soc.* **1992**, *114*, 8559-8565. (b) Perrin, C. L.; Nielson, J. B. *J. Am. Chem. Soc.* **1997**, *119*, 12734-12741. (c) Perrin, C. L.; Lau, J. S. *J. Am. Chem. Soc.* **2006**, *128*, 11820-11824.
52. The MPW1PW91/6-31+G** calculations were chosen because of their utility in NMR chemical shift calculations, (Cimino, P.; Gomez,-Paloma, L.; Duca, D.; Riccio, R.; Bifulco, G. *Magn. Reson. Chem.* **2004**, *42*, S26-S33. but more limited studies in B3LYP/6-311+G** and M06/6-31+G** calculations provided similar results.
53. The anharmonic force constant and second-order perturbation theory geometry calculations employed default procedures in Gaussian 09: Frisch, M. J.; et al. Gaussian 09, revision A.02; Gaussian, Inc.: Wallingford, CT, 2009.
54. (a) Barone, V. *J. Chem. Phys.* **2005**, *122*, 014108-014108-10. (b) Barone, V. *J. Chem. Phys.* **1994**, *101*, 10666-10676. (c) Hoy, A. R.; Mills, I. M.; Strey, G. *Mol. Phys.* **1972**, *24*, 1265-1290.
55. Intramolecular vibrational energy redistribution.
56. Altman, L. J.; Laungani, D.; Gunnarsson, G.; Wennerstrom, H.; Forsen, S. *J. Am. Chem. Soc.* **1978**, *100*, 8264-8266.
57. (a) Perrin, C. L. *Acc. Chem. Res.* **2010**, *43*, 1550-1557. (b) Perrin, C. L. *Pure Appl. Chem.* **2009**, *81*, 571-583.

APPENDIX A

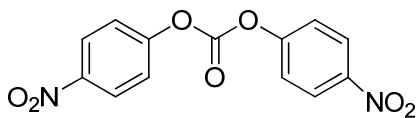
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Ethanolysis of Symmetric Aryl Carbonates

Intermolecular Starting Material ¹³C NMR KIE Sample Integration Results

for Bis-para-nitrophenyl Carbonate



1

STD1

	Average of 6 FIDs	ST. DEV.
C-O	440.1817	0.970709
carbonyl	233.9535	1.36418
"Nitro" carbon	468.621	1.543991
aryl	993.9067	1.94204
aryl	1000	0

RCVRD SM1

	Average of 6 FIDs	ST. DEV.	KIE	ST. DEV.
C-O	432.5643	0.944538	0.990	0.003
carbonyl	254.6065	0.891681	1.052	0.007
"nitro" Carbon	466.1182	1.754314	0.997	0.005
aryl	991.0472	1.364913	0.998	0.002
aryl	1000	0	1.000	0.000

STD4

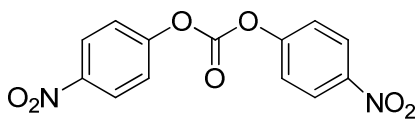
	Average of 6 FIDs	ST. DEV.
C-O	420.9783	0.202136
carbonyl	214.8412	0.639188
"Nitro" carbon	504.9205	1.163842
aryl	984.4633	0.882888
aryl	1000	0

RCVRD SM4

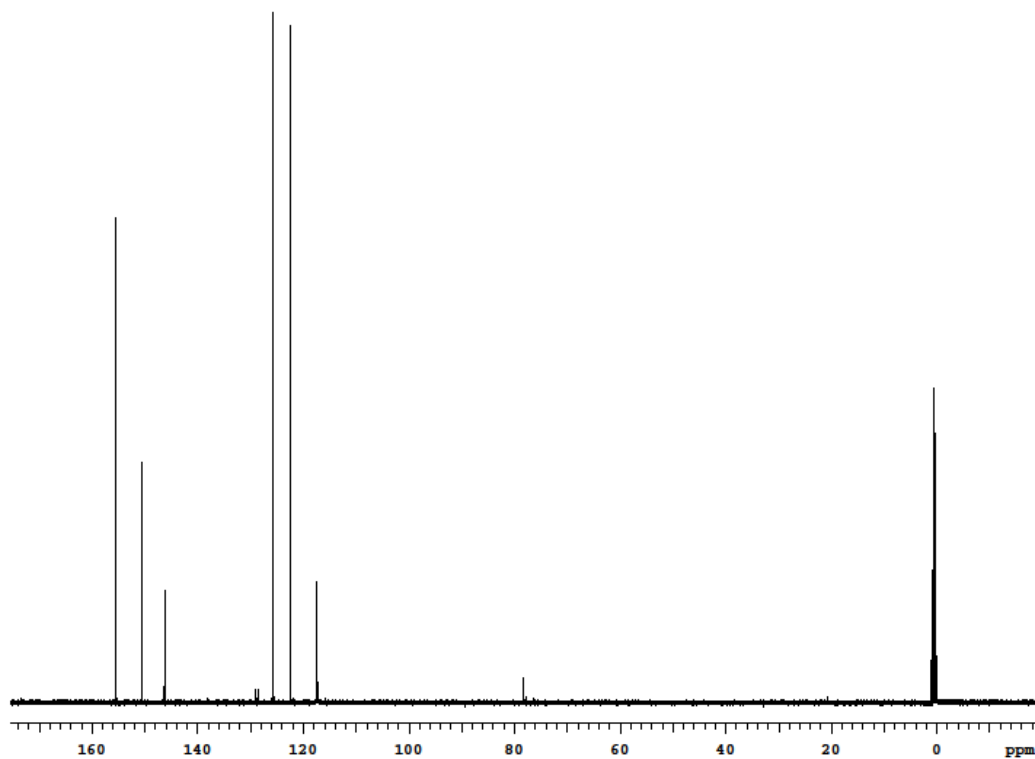
	Average of 6 FIDs	ST. DEV.	KIE4	ST. DEV.
C-O	413.1667	1.006163	0.986	0.002

	Average of 6			
	FIDs	ST. DEV.	KIE4	ST. DEV.
carbonyl	228.4117	1.519311	1.048	0.008
"nitro" Carbon	513.0562	1.063993	1.012	0.003
aryl	977.2522	0.733187	0.995	0.001
aryl	1000	0	1.000	0.000

Bis-para-nitrophenyl Carbonate – Full ^{13}C Spectrum



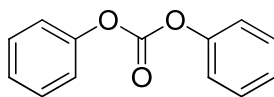
1



Intermolecular Starting Material ^{13}C NMR KIE Sample Integration Results

for Ethanolysis of Diphenyl Carbonate. All integrations are relative

integrations versus an integration of 1000 for the para-Carbon.



4

STD1

	Average of 6 FIDs	ST. DEV.
carbonyl	251.46183	0.253
C-O	483.03683	0.173
meta aryl	998.47683	0.832
ortho aryl	499.07717	0.446
para aryl	1000	0.000

RCVRD SM1

	Average of 6 FIDs	ST. DEV.	KIE	ST. DEV.
carbonyl	269.517	0.300	1.044	0.002
C-O	481.997	0.569	0.999	0.001
meta aryl	998.596	0.531	1.000	0.001
ortho aryl	501.143	0.385	1.002	0.001
para aryl	1000.000	0.000	1.000	0.000

STD2

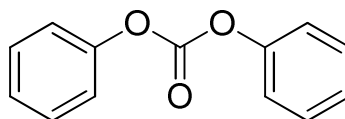
	Average of 6 FIDs	ST. DEV.
carbonyl	248.493	0.458
C-O	476.665	0.444
meta aryl	999.222	0.869
ortho aryl	497.594	0.399
para aryl	1000.000	0.000

RCVRD SM2

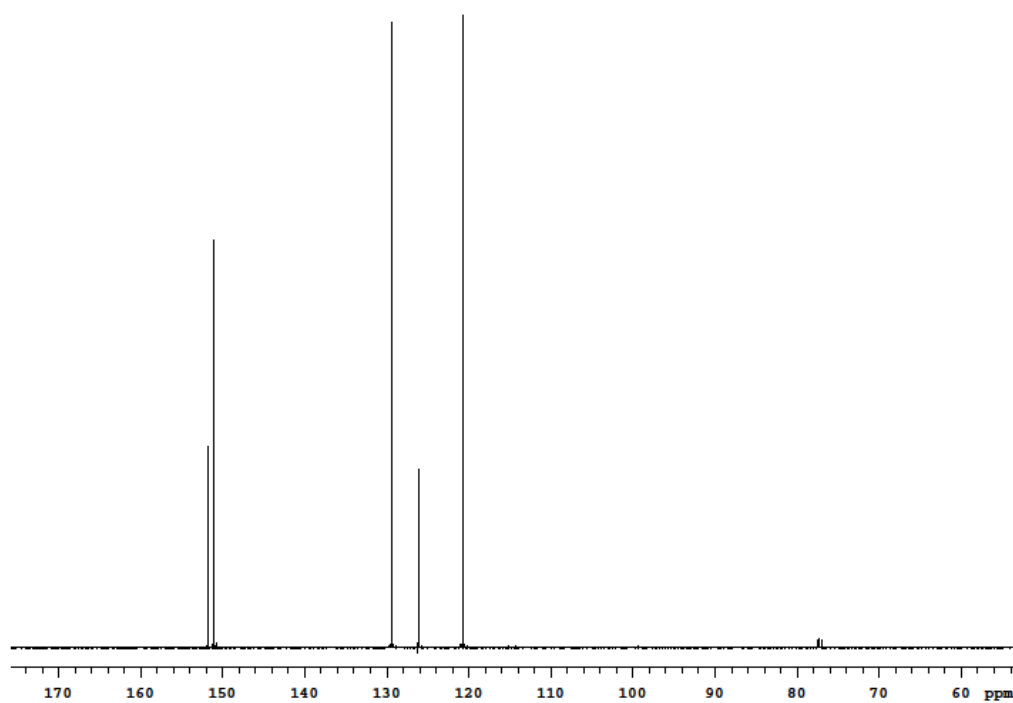
	Average of 6 FIDs	ST. DEV.	KIE	ST. DEV.
carbonyl	265.885	0.600	1.048	0.003

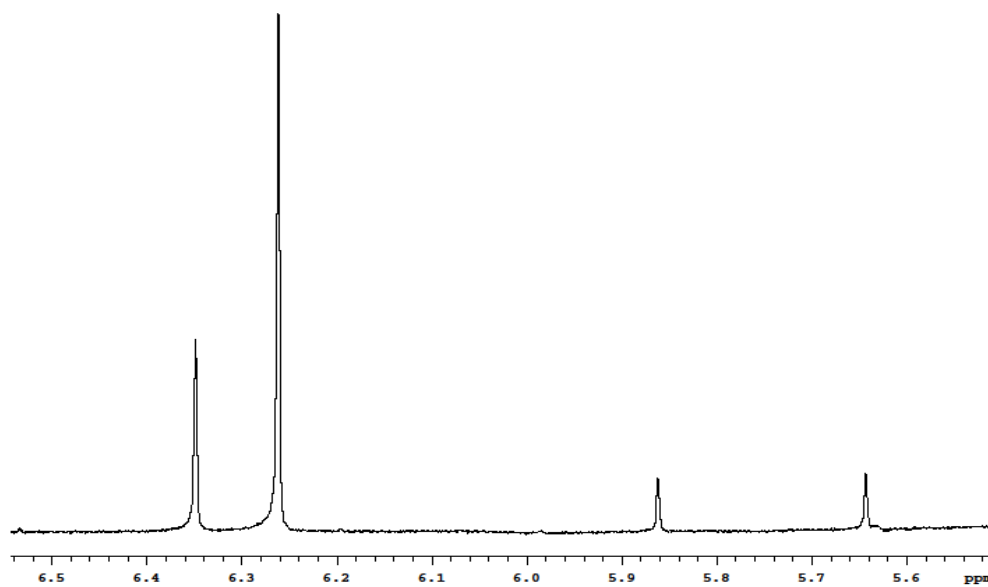
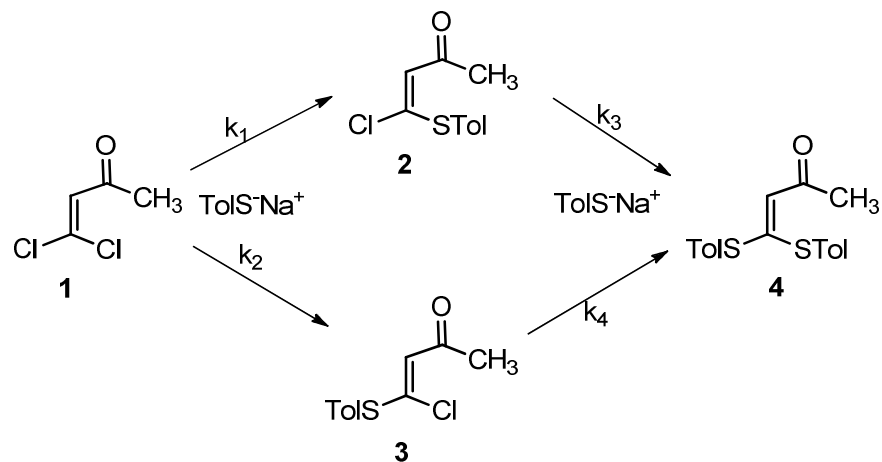
	Average of 6 FIDs	ST. DEV.	KIE	ST. DEV.
C-O	476.249	0.712	0.999	0.002
meta aryl	998.204	0.903	0.999	0.001
ortho aryl	499.404	1.096	1.002	0.002
para aryl	1000.000	0.000	1.000	0.000

Diphenyl Carbonate – Full ^{13}C spectrum



4



Dynamic Control of Stereoselectivity in a Nucleophilic Substitution Reaction **$^1\text{H-NMR}$ Spectrum of the vinylic region of the reaction mixture**

*Left most peak at 6.34 ppm represents the vinylic proton of **1**, peak at 6.26 represents vinylic proton of major product **2**, peak at 5.86 is vinylic proton of minor product **3** and peak at 5.64 is vinylic peak of disubstituted product **4**.

Mechanism of the Fujiwara Hydroarylation

Intermolecular Starting Material ^{13}C NMR KIE Sample Integration Results for Reaction of 1. All integrations are relative integrations versus an integration of 2000 for a pair of aromatic carbons.

	AVERAGE	ST. DEV.
carbonyl	935.625	1.139
quarternary(ester)	942.326	1.562
Aromatic (peak 3)	2000.000	0.000
aromatic	1013.859	2.798
aromatic	1012.544	1.906
aromatic	1010.718	0.825
aromatic	2035.464	2.452
aromatic	1017.336	1.214
aromatic	1006.180	1.249
Aromatic (C-H Act.)	1031.368	1.802
quarternary(methyl)	1015.719	1.766
acetylene	1051.718	1.673
acetylene	1034.595	2.447
methyl	961.521	1.293

RCVRD SM 1

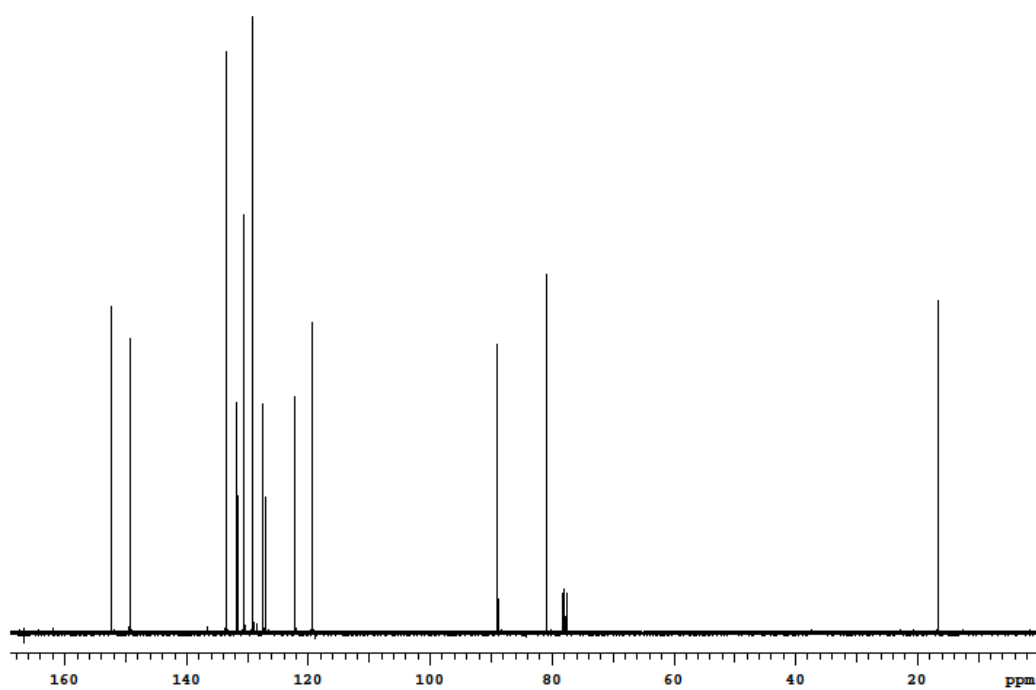
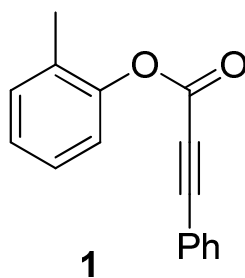
	AVERAGE	ST. DEV.	KIE	ST. DEV.
carbonyl	956.939	1.067	1.012	0.002
quarternary(ester)	939.520	2.240	0.998	0.003
Aromatic (peak 3)	2000.000	0.000	1.000	0.000
aromatic	1013.764	3.398	1.000	0.004
aromatic	1015.285	2.580	1.001	0.003
aromatic	1012.296	1.790	1.001	0.002
aromatic	2033.376	2.394	0.999	0.002
aromatic	1015.162	2.122	0.999	0.002
aromatic	1005.380	2.165	1.000	0.002

	AVERAGE	ST. DEV.	KIE	ST. DEV.
Aromatic (C-H Act.)	1059.169	2.642	1.014	0.003
quarternary(methyl)	1017.561	1.409	1.001	0.002
acetylene	1110.626	1.884	1.030	0.002
acetylene	1043.152	2.030	1.004	0.003
methyl	968.209	1.696	1.004	0.002

	Average	ST. DEV.
carbonyl	926.105	0.781
quarternary(ester)	929.951	1.053
Aromatic (peak 3)	2000.000	0.000
aromatic	1013.563	1.957
aromatic	1018.405	2.149
aromatic	1007.171	1.557
aromatic	2024.156	1.694
aromatic	1013.588	2.296
aromatic	1017.666	2.708
Aromatic (C-H Act.)	1026.615	2.131
quarternary	1015.391	1.855
acetylene	1055.979	1.201
acetylene	1028.140	1.492
methyl	946.856	1.472

RCVRD SM 3

	Average	ST. DEV.	KIE3	ST. DEV.
carbonyl	946.394	1.067	1.012	0.001
quarternary(ester)	928.567	1.669	0.999	0.002
Aromatic (peak 3)	2000.000	0.000	1.000	0.000
aromatic	1011.596	1.536	0.999	0.002
aromatic	1018.287	2.717	1.000	0.003
aromatic	1006.686	0.974	1.000	0.002
aromatic	2023.501	1.215	1.000	0.001
aromatic	1009.206	1.442	0.998	0.003
aromatic	1013.031	1.526	0.998	0.003
Aromatic (C-H Act.)	1053.897	1.047	1.014	0.002
quarternary	1017.624	0.878	1.001	0.002
acetylene	1114.293	1.658	1.029	0.002
acetylene	1034.584	0.831	1.003	0.002
methyl	950.333	1.798	1.002	0.002

Ortho-tolyl-3-phenylpropiolate – full ^{13}C spectrum

APPENDIX B

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Theoretical Structures from the Ethanolysis of Symmetric Carbonates
Bis-para-nitrophenyl carbonate

B3LYP/6-31G*

E(RB+HF-LYP) = -1136.08251998

Zero-point correction= 0.205500 (Hartree/Particle)

Thermal correction to Energy= 0.223411

Thermal correction to Enthalpy= 0.224355

Thermal correction to Gibbs Free Energy= 0.154948

Sum of electronic and ZPE= -1135.877019

Sum of electronic and thermal Energies= -1135.859109

Sum of electronic and thermal Enthalpies= -1135.858165

Sum of electronic and thermal Free Energies= -1135.927572

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 140.192	66.321	146.079

C,0,3.7049075988,-1.6503271227,0.8521503892
 C,0,2.6115510289,-1.2322128844,0.091014063
 C,0,2.6899882977,-0.1281051197,-0.7609454996
 C,0,3.8977189773,0.5577404122,-0.8565706476
 C,0,4.9881017256,0.1333789463,-0.1003091893
 C,0,4.9086568957,-0.9625688574,0.7574406659
 O,0,1.4389726915,-1.9471304406,0.3205916175
 C,0,0.5574590163,-2.1898846059,-0.6756529307
 O,0,0.6494871674,-1.8653580973,-1.8296476514
 N,0,6.2591916117,0.8649198532,-0.2064011514
 O,0,7.2030575593,0.4684437175,0.47650434
 O,0,-0.4500713455,-2.8770490862,-0.0915542615
 C,0,-1.5456594404,-3.3204015109,-0.8276822391
 C,0,-2.755235735,-3.3126635367,-0.1302247111
 C,0,-3.9025700155,-3.801411689,-0.7432008055
 C,0,-3.8098760205,-4.2897093497,-2.0455542177
 C,0,-2.6036995823,-4.3051867712,-2.7425770325
 C,0,-1.452480495,-3.8187137033,-2.1292366054
 N,0,-5.020282721,-4.8071799411,-2.7007020295
 O,0,-6.0697221298,-4.7836163748,-2.0583955229
 O,0,-4.9097993344,-5.232224581,-3.8500303733
 O,0,6.3011767891,1.8283105004,-0.9705617367
 H,0,3.5965995623,-2.5066326502,1.5088609913
 H,0,5.7776798641,-1.2596655115,1.3308451722
 H,0,4.0020110719,1.4175690267,-1.5065311469
 H,0,1.8351620554,0.1831934705,-1.3452669419

H,0,-2.7799880084,-2.9260546645,0.8827805587
 H,0,-4.8578737768,-3.8089974433,-0.2336940189
 H,0,-2.5758213469,-4.6984643783,-3.7511334797
 H,0,-0.5090189614,-3.8170226072,-2.657384605

Transition State

B3LYP/6-31G*

E(RB+HF-LYP) = -1251.23555529

Zero-point correction= 0.244764 (Hartree/Particle)
 Thermal correction to Energy= 0.265388
 Thermal correction to Enthalpy= 0.266332
 Thermal correction to Gibbs Free Energy= 0.192572
 Sum of electronic and ZPE= -1251.012050
 Sum of electronic and thermal Energies= -1250.991426
 Sum of electronic and thermal Enthalpies= -1250.990482
 Sum of electronic and thermal Free Energies= -1251.064241

E CV S

KCal/Mol Cal/Mol-K Cal/Mol-K

Total 166.533 76.689 155.240
 Zero-point correction= 0.243550 (Hartree/Particle)
 Thermal correction to Energy= 0.264319
 Thermal correction to Enthalpy= 0.265263
 Thermal correction to Gibbs Free Energy= 0.191367
 Sum of electronic and ZPE= -1250.992005
 Sum of electronic and thermal Energies= -1250.971237
 Sum of electronic and thermal Enthalpies= -1250.970293
 Sum of electronic and thermal Free Energies= -1251.044189

E CV S

KCal/Mol Cal/Mol-K Cal/Mol-K

Total 165.862 76.182 155.527

C,0,3.2787205984,-1.6352809188,-0.5914464899
 C,0,2.3296522542,-0.8673686983,0.0880679058
 C,0,2.6531157746,0.3303327073,0.7316903022
 C,0,3.9719173194,0.7671540564,0.6742193724
 C,0,4.9262521567,0.005685798,-0.0110340198
 C,0,4.595958288,-1.1950071519,-0.6441816173
 O,0,1.0563090929,-1.3878763703,0.2142611177
 C,0,-0.0005317251,-0.6901641816,-0.3062040785
 O,0,0.064687643,1.2541187277,1.4723147758

C,0,0.1044053009,2.4535389318,0.8111736718
 N,0,6.311482636,0.466588567,-0.0630006318
 O,0,6.5958796673,1.5298499378,0.4958662321
 O,0,-1.1009291311,-1.3161741307,0.2151348559
 C,0,-2.3370423995,-0.7123693905,0.089809262
 C,0,-3.3354842329,-1.4157722376,-0.5887896984
 C,0,-4.620656971,-0.8891009133,-0.6406276164
 C,0,-4.8700849214,0.3309794123,-0.0075214629
 C,0,-3.8668122503,1.0275904081,0.676831956
 C,0,-2.5798432877,0.5042680266,0.7333934135
 N,0,-6.2217294888,0.8827475639,-0.0585525681
 O,0,-7.0934450989,0.2409887617,-0.6572899883
 O,0,0.0240319287,0.0601881285,-1.2417151473
 O,0,-6.4345869659,1.962535503,0.5004541011
 O,0,7.1382959048,-0.2315469063,-0.6623466172
 H,0,-1.7119407951,0.9564992157,1.2586000736
 H,0,-4.1106234963,1.9650484994,1.1622029746
 H,0,-5.4243062111,-1.3975909788,-1.1581365913
 H,0,-3.0954726633,-2.3612480855,-1.0647114883
 H,0,2.9761571544,-2.5626346464,-1.0673682795
 H,0,5.3637141241,-1.7555619751,-1.1624085096
 H,0,4.2777416254,1.6862672208,1.1595641137
 H,0,1.8175298107,0.8390950001,1.2575790226
 H,0,-0.772812167,2.6369892024,0.1385461353
 H,0,0.134364865,3.343686613,1.4913514228
 H,0,0.9913296609,2.5781883033,0.1378080958

Diphenyl Carbonate

Diphenyl carbonate opt

B3LYP/6-31G*

E(RB+HF-LYP) = -727.081978901

Zero-point correction= 0.200365 (Hartree/Particle)

Thermal correction to Energy= 0.213183

Thermal correction to Enthalpy= 0.214128

Thermal correction to Gibbs Free Energy= 0.157800

Sum of electronic and ZPE= -726.881614

Sum of electronic and thermal Energies= -726.868796

Sum of electronic and thermal Enthalpies= -726.867851

Sum of electronic and thermal Free Energies= -726.924179

E CV S
 KCal/Mol Cal/Mol-K Cal/Mol-K
 Total 133.775 49.249 118.551

C,0,-2.1921101965,-2.6556949327,-2.0859672799
 C,0,-1.8463697426,-2.9222567106,-0.7624279847
 C,0,-2.4083415283,-3.9874504665,-0.0630964433
 C,0,-3.3445796861,-4.801654215,-0.700313266
 C,0,-3.7117810787,-4.547109666,-2.0229131324
 C,0,-3.1340914259,-3.4765436812,-2.7080422329
 O,0,-0.8542789315,-2.2095580269,-0.0787684437
 C,0,-0.8247477467,-0.8597011061,-0.1358267837
 O,0,-1.5850946196,-0.1368937688,-0.726357381
 O,0,0.237887821,-0.4940657875,0.6147502617
 C,0,0.5612852315,0.8594475878,0.7663430814
 C,0,0.6121830468,1.7488973222,-0.305402269
 C,0,1.027366797,3.0597337238,-0.0657611613
 C,0,1.392308471,3.4698516423,1.2179286053
 C,0,1.342329989,2.5601669365,2.2756982943
 C,0,0.9247967278,1.2480153639,2.053351177
 H,0,-4.4428855228,-5.1799522495,-2.5177336593
 H,0,1.7150446989,4.4922561137,1.3922312244
 H,0,-2.1038174379,-4.1661117929,0.9631006796
 H,0,-3.7859169233,-5.6341095807,-0.1595377053
 H,0,-3.4141119504,-3.2745035903,-3.7381521018
 H,0,-1.7470433706,-1.8211723314,-2.6126398556
 H,0,0.8802106025,0.5210952408,2.8579226528
 H,0,1.6272656121,2.8685486338,3.2776517765
 H,0,1.066103012,3.7623528343,-0.8935194585
 H,0,0.3227471513,1.4296545069,-1.2984825949

Transition State

Diphenyl carbonate w/ methoxide ts search
 B3LYP/6-31G*
 E(RB+HF-LYP) = -842.206364553

Zero-point correction= 0.238054 (Hartree/Particle)
 Thermal correction to Energy= 0.253835
 Thermal correction to Enthalpy= 0.254779
 Thermal correction to Gibbs Free Energy= 0.193372
 Sum of electronic and ZPE= -841.968372
 Sum of electronic and thermal Energies= -841.952591

Sum of electronic and thermal Enthalpies= -841.951647
 Sum of electronic and thermal Free Energies= -842.013054

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	159.284	59.343 129.242
Zero-point correction=	0.238062 (Hartree/Particle)	
Thermal correction to Energy=	0.253888	
Thermal correction to Enthalpy=	0.254832	
Thermal correction to Gibbs Free Energy=	0.192695	
Sum of electronic and ZPE=	-841.968302	
Sum of electronic and thermal Energies=	-841.952477	
Sum of electronic and thermal Enthalpies=	-841.951533	
Sum of electronic and thermal Free Energies=	-842.013670	

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	159.317	59.401 130.779

C,0,-1.2784899071,-4.3492254033,-1.1706209789
 C,0,-1.6317673933,-3.0712842761,-0.7336974596
 C,0,-2.9240443168,-2.5731551657,-0.8913537129
 C,0,-3.89169722,-3.3715276828,-1.507119183
 C,0,-3.5597968134,-4.6501833672,-1.9588537032
 C,0,-2.2555896954,-5.129494739,-1.7879230357
 O,0,-0.7189390376,-2.3151403733,-0.0177173929
 C,0,0.3912142289,-1.8318536061,-0.669574614
 O,0,0.4639406284,-1.5509477459,-1.8388401637
 O,0,1.150893779,-1.2984453795,0.3443624402
 C,0,2.4348187354,-0.8660302535,0.056786401
 C,0,3.4276374741,-1.8014037357,-0.2405424127
 C,0,4.7345018578,-1.3451801391,-0.4101536819
 C,0,5.047279036,0.0130461746,-0.2786006027
 C,0,4.0385915057,0.929065589,0.0257062684
 C,0,2.7222561986,0.4909593405,0.1939677823
 O,0,1.5714390101,-3.9643834094,-0.7553117364
 C,0,1.9522489387,-4.186689202,-2.0490274492
 H,0,6.071856504,0.3554266617,-0.4118467195
 H,0,-4.3134881618,-5.2703547023,-2.4405716196
 H,0,3.0874652623,-2.8436181757,-0.3214152513
 H,0,5.5217354637,-2.0592482307,-0.6447077685
 H,0,4.2720947995,1.9868893637,0.1306049406
 H,0,1.9196160812,1.1832683829,0.4322525514
 H,0,-3.1570782364,-1.5752319876,-0.5305806538

H,0,-4.9031460039,-2.9904625169,-1.6347169606
 H,0,-1.9980497621,-6.127629318,-2.1373527928
 H,0,-0.2342747056,-4.6405384409,-0.9893327916
 H,0,1.1116201223,-4.174003037,-2.7895088883
 H,0,2.6797773182,-3.4358587793,-2.4549194748
 H,0,2.4549283096,-5.1798608452,-2.2046753361

ONIOM trajectories of Trimethoxy Methoxide

ONIOM(B3LYP/6-31G*:AM1)

Zero-point correction= 1.607135 (Hartree/Particle)

Thermal correction to Energy= 1.719606

Thermal correction to Enthalpy= 1.720550

Thermal correction to Gibbs Free Energy= 1.420936

Sum of electronic and ZPE= -0.729439

Sum of electronic and thermal Energies= -0.616968

Sum of electronic and thermal Enthalpies= -0.616024

Sum of electronic and thermal Free Energies= -0.915638

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 1079.069	355.814	630.591

C	0.1680364	-1.3162941	0.2505533
O	-0.4047970	-0.2718881	0.6915328
O	1.4182249	-1.7041487	0.8754109
C	2.0854343	-0.7084610	1.6325596
H	2.9869436	-0.4712586	1.0773129
H	1.4277658	0.1585875	1.8835444
H	2.3908560	-1.0061812	2.6535713
O	-0.5596811	-2.5026548	0.2268028
C	-1.5483015	-2.5509805	1.2099074
H	-1.1497420	-2.6706125	2.2635642
H	-2.1579363	-1.6579593	1.2326818
H	-2.1765143	-3.4275344	0.9117935
O	0.6208489	-1.1976467	-1.2050965
C	-0.4179589	-1.0240303	-2.1013867
H	-1.3882095	-0.7155588	-1.7275582
H	-0.1539894	-0.1054038	-2.7295892
H	-0.6290238	-1.9840647	-2.7661913
H	-2.5782894	-5.8676231	3.1293377

O -2.6504939 -6.6069563 3.7311288 M
C -1.7379438 -6.4449143 4.7895423 M
C -1.3765088 -4.9898460 5.0470296 M
H -2.2374951 -6.9596707 5.6480613 M
H -0.7952622 -6.9454131 4.4904379 M
H -1.6106077 -4.3634819 4.1583652 M
H -1.9428576 -4.5501950 5.9527889 M
H -0.3335355 -4.7602026 5.2010524 M
H -1.8529553 1.0827243 1.1908810 M
O -2.6396999 1.4383051 1.6217447 M
C -2.5794809 2.8724812 1.7347944 M
C -2.1696749 3.5975733 0.4927689 M
H -3.6550143 3.0420164 1.9132210 M
H -1.8559836 3.1407914 2.5661864 M
H -2.4951480 4.6475633 0.6472649 M
H -1.1046031 3.6259142 0.3267561 M
H -2.6101880 3.2361255 -0.4387480 M
H -5.0897766 -3.3605585 -2.6183810 M
O -5.5846640 -4.1980146 -2.4961614 M
C -5.2829885 -5.1001755 -3.5018964 M
C -3.7689348 -5.2310365 -3.7832400 M
H -5.7761712 -6.0960809 -3.2423854 M
H -5.7598824 -4.7437989 -4.4195520 M
H -3.5151230 -4.9629568 -4.8059449 M
H -3.2048221 -4.5204080 -3.0933630 M
H -3.3903728 -6.2688496 -3.5481900 M
H -3.9029789 0.0691602 0.8372681 M
O -4.5225292 -0.6620110 1.1407654 M
C -4.6465631 -0.4592203 2.5257228 M
C -6.0728911 -0.1982298 2.9841701 M
H -4.2499297 -1.3994195 3.0247516 M
H -4.0182876 0.4042034 2.8956600 M
H -6.7788776 -0.2205635 2.1436531 M
H -6.3299586 -1.0155221 3.7111874 M
H -6.1548555 0.8041455 3.4764710 M
H -6.4016662 -1.0266071 -1.5524235 M
O -6.0856329 -0.7973623 -2.4752028 M
C -4.7242654 -0.5963296 -2.2314854 M
C -3.9665075 -0.5039345 -3.5700447 M
H -4.5943564 0.3756787 -1.6185388 M
H -4.3549569 -1.5584019 -1.7350013 M
H -4.3760685 0.3908494 -4.1019502 M
H -2.8842827 -0.3065941 -3.4416925 M
H -4.2024406 -1.4294466 -4.2443364 M

H -4.4814555 -6.3739879 -1.4745802 M
O -3.9879543 -6.8665276 -0.8136554 M
C -3.7685179 -6.1702864 0.3802660 M
C -5.0611195 -5.7243368 1.0612641 M
H -3.2458061 -6.9367232 1.0807471 M
H -3.1373584 -5.2991976 0.2579675 M
H -5.0409165 -5.6381248 2.2039132 M
H -5.4433293 -4.7474616 0.6805345 M
H -5.8345074 -6.5742472 0.9198613 M
H -2.7311579 1.7158382 4.2196324 M
O -2.7841077 1.4853854 5.1246189 M
C -2.5064227 2.6497146 5.8885351 M
C -1.4571196 3.5797112 5.3601497 M
H -3.4832439 3.1182857 6.0251502 M
H -2.1807054 2.1625527 6.9035229 M
H -1.2744503 4.2996439 6.1498140 M
H -0.5194036 3.0759202 5.0904374 M
H -1.7896550 4.1258706 4.4521164 M
H -1.3517660 5.4056491 -3.7653424 M
O -1.1158495 5.3074347 -4.6979607 M
C -0.8431708 3.9599213 -4.9751337 M
C -0.2105321 3.9878845 -6.3769862 M
H -0.1799300 3.5820376 -4.2041708 M
H -1.7991003 3.3468395 -4.9679579 M
H -0.4359894 3.0059525 -6.9009122 M
H -0.7619586 4.7740656 -6.9485653 M
H 0.8697552 4.2307777 -6.2250469 M
H -3.0628712 6.5692949 -4.3865426 M
O -2.9987843 6.6096318 -3.4442825 M
C -3.8979019 5.6308073 -2.9633945 M
C -5.3178006 6.0174955 -3.1878462 M
H -3.6407393 4.6717146 -3.4950648 M
H -3.6007784 5.5402921 -1.8653767 M
H -5.9119014 5.1213389 -2.9461719 M
H -5.6260506 6.8629231 -2.5178883 M
H -5.4658799 6.3259305 -4.2593873 M
H 3.0109641 -3.3545207 1.5831470 M
O 3.3054872 -3.9967500 2.2127287 M
C 2.0714605 -4.6290526 2.6154582 M
C 1.4164604 -5.2955280 1.4283186 M
H 1.4094025 -3.7985837 3.0191941 M
H 2.3617328 -5.3393366 3.4109979 M
H 0.7480804 -4.5871287 0.8753752 M
H 0.8462320 -6.2555852 1.5407166 M

H 2.2251005 -5.6002310 0.7098058 M
H 3.0566980 -2.2409751 -0.7435050 M
O 3.7695500 -2.7102358 -1.2866608 M
C 4.5744704 -1.7197350 -1.9769127 M
C 5.0095797 -0.7109255 -0.8708914 M
H 3.9943077 -1.3565266 -2.8420586 M
H 5.4306546 -2.3046935 -2.3113693 M
H 4.1569291 -0.0853160 -0.4981574 M
H 5.8687443 -0.1525546 -1.1588569 M
H 5.3228001 -1.3568064 -0.0013385 M
H 3.0074590 -4.0649031 -2.8371750 M
O 2.9548320 -4.7202145 -3.5342022 M
C 1.6434785 -4.5444606 -4.1034313 M
C 0.6116291 -5.2678050 -3.2870753 M
H 1.7019611 -5.0599854 -5.0768334 M
H 1.4827271 -3.4394913 -4.2477628 M
H -0.1500008 -5.8794797 -3.8822258 M
H -0.0152344 -4.5268400 -2.7108596 M
H 1.1323118 -5.9768007 -2.5795619 M
H 4.3549672 -2.9858673 4.5473363 M
O 4.5869690 -2.5078650 5.3030917 M
C 5.7863307 -1.7852596 4.9423756 M
C 5.8682920 -1.6791787 3.4217424 M
H 6.7172852 -2.3273018 5.4097880 M
H 5.7487475 -0.7601858 5.3773611 M
H 6.9094305 -1.4667313 3.0238943 M
H 5.1702641 -0.8583014 3.0690111 M
H 5.5884117 -2.6079399 2.9087714 M
H 1.2725914 1.7503453 4.0254366 M
O 1.8029904 1.9998969 4.8294986 M
C 2.9722555 1.1886827 4.8239924 M
C 2.8718786 0.2834210 6.0588219 M
H 3.8649559 1.9482974 4.9187158 M
H 3.1168985 0.5494117 3.9211595 M
H 2.2726667 -0.6235179 5.7662959 M
H 2.3993271 0.7764743 6.9442171 M
H 3.8439960 -0.0876113 6.4133187 M
H 0.3509690 1.6002761 0.3836793 M
O 0.8682632 2.4044617 0.5005884 M
C 1.6943255 2.4554141 -0.6506147 M
C 0.8967548 2.9242604 -1.8574048 M
H 2.1512480 1.4331380 -0.8609450 M
H 2.5176956 3.1439790 -0.2833968 M
H 1.7143646 3.2577361 -2.6526621 M

H 0.2730543 3.7994256 -1.6083814 M
 H 0.2752738 2.0591926 -2.2405077 M
 H 5.9484153 -4.1863777 -1.6605881 M
 O 6.6435964 -4.6254711 -1.1763327 M
 C 6.0601268 -5.1760695 0.0023688 M
 C 4.7503865 -5.9338074 -0.1600524 M
 H 6.8061964 -5.8776989 0.4519303 M
 H 5.8586141 -4.3135208 0.6636001 M
 H 4.2947207 -6.0954050 0.8542835 M
 H 4.0757824 -5.2589396 -0.7741690 M
 H 4.8537689 -6.9404818 -0.6086359 M
 H 4.8237697 5.1560824 -1.3817754 M
 O 4.1758214 5.5019725 -2.0261895 M
 C 4.6889497 5.1049572 -3.3126242 M
 C 3.5874264 5.4647228 -4.2959101 M
 H 5.5586750 5.7382214 -3.5655172 M
 H 4.9597877 4.0261686 -3.2860822 M
 H 3.7588011 5.1298114 -5.3306948 M
 H 2.6327842 5.0168022 -3.8881750 M
 H 3.4408580 6.5866534 -4.2697312 M
 H 5.4204392 3.8653175 0.6337666 M
 O 6.0305434 4.5722397 0.7177126 M
 C 5.4575235 5.5611142 1.5460393 M
 C 4.0206533 5.9340935 1.1643710 M
 H 5.4891700 5.2635528 2.5830058 M
 H 6.2211789 6.3798913 1.4930678 M
 H 3.6369985 6.7527937 1.7368591 M
 H 4.0103327 6.2813002 0.0808976 M
 H 3.3365918 5.0877927 1.1892042 M

ONIOM Trajectories of Dimethoxy Nitrophenoxy Methoxide

ONIOM(B3LYP/6-31G*:AM1)
 Zero-point correction= 1.668361 (Hartree/Particle)
 Thermal correction to Energy= 1.785818
 Thermal correction to Enthalpy= 1.786762
 Thermal correction to Gibbs Free Energy= 1.476444
 Sum of electronic and ZPE= -0.632700
 Sum of electronic and thermal Energies= -0.515243
 Sum of electronic and thermal Enthalpies= -0.514298
 Sum of electronic and thermal Free Energies= -0.824617

E CV S

KCal/Mol Cal/Mol-K Cal/Mol-K
Total 1120.618 376.509 653.121

C 2.3107020 2.8541239 0.3428389
O 0.8618821 2.7884030 0.3809869
C 0.4126910 1.5397121 0.8907788
O 0.6804859 2.1398360 2.5966147
C 0.6148726 1.3186551 3.5961458
O 1.0398199 0.5118020 0.7218348
O -0.9462208 1.7224717 0.7006236
C -1.8616582 0.6668220 1.0247486
C 0.0272074 0.0302841 3.4906324
C -0.1537528 -0.7578177 4.6194349
C 0.4027894 -0.3771850 5.8430495
C 1.1704472 0.7822241 5.9239961
C 1.2125430 1.6818660 4.8243746
H -0.1557407 -0.4288268 2.6081032
H -0.7579858 -1.6602789 4.6188658
N 0.3416742 -1.2654063 6.9714026
H 1.6821766 1.1341361 6.8741892
H 1.6012740 2.6796910 4.7487782
H 2.6248668 3.0610540 1.3294311
H 2.7683821 1.9068981 -0.0531575
H 2.5092842 3.6619612 -0.3428761
H -2.8383313 0.8429794 0.5508038
H -1.4420291 -0.2763582 0.6563713
H -1.9989076 0.6865865 2.0952070
O 1.1215221 -1.0754613 7.9070014
O -0.5421136 -2.1306852 6.9516973
O 0.5776254 -0.6620742 -2.0895306 M
C 1.4212806 -1.7577503 -1.8082639 M
C 1.3168522 -2.3095560 -0.4167418 M
O -1.3188195 -1.2933677 -4.2337880 M
C -1.9190556 -0.4013622 -3.3163474 M
C -3.3591919 -0.1594001 -3.7192458 M
O 3.6426838 -0.4786021 -0.0840246 M
C 4.2063782 -0.5151276 1.2030395 M
C 3.4262532 -1.4898191 2.0970151 M
O -0.2167959 4.3073591 -2.3687552 M
C -1.1023404 3.3156344 -2.8650798 M
C -1.9951101 2.6100253 -1.8800463 M
O -1.7076647 4.6233203 1.1111245 M
C -1.2967024 5.5484110 2.1261908 M
C 0.0732646 5.2547930 2.6895627 M

O -5.0862477 4.1913208 1.4556601 M
C -4.9433701 4.1605795 2.9152471 M
C -3.9518016 3.0653830 3.2726028 M
C -2.0776069 -2.5656879 -0.0597830 M
C -1.6329522 -3.9577760 0.4267100 M
O -2.8530988 -2.7033676 -1.2530473 M
C -3.7389411 6.0392967 -1.6665754 M
C -2.4558066 6.8336034 -2.0768269 M
O -1.5217569 6.9781162 -1.0108896 M
O -4.7088157 -4.7048395 0.2609048 M
C -5.5325154 -5.1385410 1.3224681 M
C -5.8795819 -4.0209455 2.2969718 M
O -7.1709505 -4.4516254 -1.8610584 M
C -6.7310395 -3.5218117 -2.8370974 M
C -5.3207799 -3.8954401 -3.2094105 M
O 0.9701501 0.7438506 -4.7535748 M
C 1.2849984 -0.1102650 -5.8521990 M
C 2.4177627 -1.0783405 -5.5380152 M
O -5.4036812 -1.6215361 -0.1910737 M
C -5.7235331 -0.3851471 0.4277407 M
C -5.2995148 0.9089216 -0.3319666 M
C 2.5162997 6.0036889 -0.4765466 M
C 2.5156670 6.2242496 -1.9468904 M
O 2.3809497 5.0152176 -2.6642164 M
C 3.4699480 2.2536258 -3.1191150 M
C 4.7860855 1.6032363 -3.5014131 M
O 4.5787757 0.1673850 -3.7020615 M
C 3.1056187 -5.1004590 2.9973698 M
C 2.7014431 -6.5184685 3.5150550 M
O 3.6880351 -5.2359119 1.6576233 M
O 2.2864474 -6.1293775 -1.5021788 M
C 1.3823034 -5.5545046 -0.5736603 M
C 0.5810704 -6.5820510 0.2111911 M
O 7.1991890 -1.3312961 -0.7507433 M
C 6.6021393 -0.2145848 -1.3909933 M
C 6.9993078 1.0385869 -0.5976200 M
C 4.6223462 -3.6895137 -1.0658673 M
C 5.2904312 -4.2529666 -2.2928019 M
O 5.7628805 -3.1997471 -3.0979289 M
H -4.4590575 -1.6102550 -0.4111545 M
H -6.8695333 -0.4093806 0.5541155 M
H -5.1579589 -0.2311953 1.4199940 M
H -4.3993321 0.7182938 -0.9113345 M
H -6.0608912 1.3962296 -1.0544002 M

H -5.0623390 1.6692466 0.4352084 M
H 0.3029866 -0.2835259 -1.2372001 M
H 1.2832427 -2.4670738 -2.6237321 M
H 2.4277001 -1.3754064 -2.0147001 M
H 2.3448407 -2.5819166 -0.0963935 M
H 0.9613122 -1.5323396 0.3120246 M
H 0.5816886 -3.1794645 -0.3021517 M
H -4.4958852 -3.7830821 0.5317915 M
H -6.4026306 -5.6068874 0.9128359 M
H -4.9606929 -5.9805031 1.7902947 M
H -6.6268107 -4.3647153 2.9884715 M
H -5.0067409 -3.8079715 2.9576471 M
H -6.1477560 -3.0896579 1.8001189 M
H -0.3625655 -1.2701941 -3.9287939 M
H -1.9322733 -0.8725353 -2.2988486 M
H -1.3957460 0.5668700 -3.4040726 M
H -3.9813542 -0.9519365 -3.2709824 M
H -3.7920294 0.7544766 -3.3548828 M
H -3.6154957 -0.1658601 -4.8469166 M
H -2.3837192 -3.2240490 -1.9017377 M
H -1.1630493 -1.9809334 -0.2592744 M
H -2.8292713 -2.0861764 0.6732250 M
H -0.8929215 -4.3945613 -0.2775214 M
H -1.1936051 -3.8512356 1.4381815 M
H -2.4740164 -4.6302739 0.5918570 M
H -6.4797481 -4.5516123 -1.1918242 M
H -7.4743851 -3.5359190 -3.6813596 M
H -6.7940680 -2.5064905 -2.3185129 M
H -4.6721378 -3.0997687 -3.6460020 M
H -4.8106647 -4.3932306 -2.3431561 M
H -5.2674036 -4.6905166 -4.0341028 M
H 1.1204356 0.2260977 -3.9466456 M
H 0.3477090 -0.6565245 -6.0858153 M
H 1.6138672 0.5581905 -6.6337500 M
H 2.5606480 -1.7182811 -6.4578561 M
H 3.3388293 -0.5800997 -5.2901082 M
H 2.0855645 -1.7634395 -4.6640553 M
H 4.4666477 -4.6662231 1.5594965 M
H 3.8850234 -4.6795461 3.6301648 M
H 2.2494739 -4.3638098 2.9599848 M
H 2.0169752 -6.3600158 4.3814013 M
H 2.2508257 -6.9372898 2.6714609 M
H 3.7020348 -6.9775402 3.7322707 M
H 2.7101007 -6.8965643 -1.1092904 M

H 1.9579968 -4.9560592 0.2044401 M
H 0.7308672 -4.8853893 -1.1581865 M
H -0.1941835 -6.1039540 0.8872466 M
H 0.1095702 -7.2656212 -0.5300816 M
H 1.3120490 -7.1788809 0.8098836 M
H 0.4815462 3.9882224 -1.7693359 M
H -0.5517119 2.5543836 -3.4073309 M
H -1.7491184 3.9521869 -3.5614321 M
H -1.8203122 1.5306119 -1.7852493 M
H -3.0624025 2.7403233 -2.0423813 M
H -1.8561846 3.0542826 -0.8312775 M
H -1.2001633 3.8325112 1.1352575 M
H -2.1030834 5.5317016 2.9315844 M
H -1.3149275 6.6076899 1.6558724 M
H -0.1021398 4.4985412 3.4922214 M
H 0.4889596 6.2047792 3.0923527 M
H 0.6597671 4.8253228 1.8640014 M
H -4.2010898 4.4261643 1.0908278 M
H -5.9012669 3.7606236 3.2009506 M
H -4.7332603 5.1709889 3.3664210 M
H -3.9736882 2.9901908 4.3570759 M
H -2.9216065 3.2469595 2.8925978 M
H -4.4053692 2.1083382 2.8272690 M
H 1.6308817 5.1065177 -3.2554487 M
H 1.6966620 6.9081097 -2.2505052 M
H 3.5230243 6.6944852 -2.2328219 M
H 2.5428840 6.9364496 0.1132382 M
H 3.4314314 5.4542285 -0.2392401 M
H 1.6623853 5.3115261 -0.2576173 M
H 4.2529174 -0.0432436 -2.8099908 M
H 5.2188107 1.8989280 -4.4638894 M
H 5.6107162 1.6398076 -2.7237466 M
H 3.1378473 2.0511303 -2.0759355 M
H 2.5829544 2.0002437 -3.7760278 M
H 3.7198942 3.2964840 -3.0288359 M
H 2.7855955 -0.0890666 -0.0798773 M
H 4.0724084 0.5104457 1.7251262 M
H 5.2710887 -0.7338757 1.1255992 M
H 3.7610824 -1.2708706 3.0840677 M
H 3.5188626 -2.5663671 1.7305272 M
H 2.3600830 -1.3389472 1.8808230 M
H -1.3060974 6.0780457 -0.7586003 M
H -2.8182337 7.8745471 -2.2584307 M
H -1.9618587 6.3424726 -2.9575121 M

H -4.3510831 5.7437328 -2.5656620 M
 H -3.5455277 5.1163580 -1.0859004 M
 H -4.4517840 6.6913681 -1.0552772 M
 H 6.9043613 -2.1009566 -1.2730305 M
 H 6.9726347 -0.0678893 -2.4421266 M
 H 5.4700696 -0.3214635 -1.4156257 M
 H 6.4562596 1.9087062 -1.0288219 M
 H 6.6752485 0.8972757 0.4633499 M
 H 8.0837443 1.2341080 -0.7181560 M
 H 5.0061194 -2.8156123 -3.5739118 M
 H 4.4840032 -4.8298553 -2.7642855 M
 H 6.2082797 -4.8522512 -2.1006828 M
 H 3.9510076 -4.3615288 -0.5331184 M
 H 5.4552887 -3.4598864 -0.3520848 M
 H 3.9631847 -2.8775415 -1.4243695 M

Becke/6-31G* opt of dimethyl carbonate

B3LYP opt of dimethyl carbonate

B3LYP/6-31G*

E(RB+HF-LYP) = -343.607745645

C 0.97231 0.26601 1.37748
 O 0.57419 -0.71719 0.4638
 C -0.65251 -1.46741 0.66578
 O -0.87425 -2.04615 1.72102
 O -0.6383 -2.18554 -0.59609
 C -1.71907 -2.99076 -0.97499
 H 1.91136 0.70849 1.04836
 H 0.20737 1.03896 1.43525
 H 1.10789 -0.18464 2.35955
 H -1.51502 -3.43866 -1.94642

Theoretical structures from Dynamic Control of Stereoselectivity in a Nucleophilic Substitution Reaction.

dichloroSM2

betabeta dichlorovinyl ketone opt

B3LYP/6-31G*

E(RB+HF-LYP) = -1150.41639172

Zero-point correction= 0.071876 (Hartree/Particle)
 Thermal correction to Energy= 0.079499
 Thermal correction to Enthalpy= 0.080443
 Thermal correction to Gibbs Free Energy= 0.038345
 Sum of electronic and ZPE= -1150.344516
 Sum of electronic and thermal Energies= -1150.336893
 Sum of electronic and thermal Enthalpies= -1150.335948
 Sum of electronic and thermal Free Energies= -1150.378046

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 49.886	25.663	88.602

Cl,0,1.5571925207,-2.6060256961,-1.9100975868
 C,0,2.8763090896,-3.2930648213,-2.8228149833
 Cl,0,3.875719019,-4.3534516879,-1.8770988641
 C,0,3.0379638685,-2.9865504897,-4.1187112107
 C,0,4.0518880156,-3.4124660028,-5.1293496421
 O,0,3.9292827932,-2.9497408755,-6.2537956273
 C,0,5.1793950049,-4.3662354962,-4.7973241032
 H,0,4.7941146832,-5.3305347216,-4.4488706819
 H,0,5.7738762917,-4.5130541675,-5.7009332029
 H,0,5.8146175283,-3.9671996334,-3.9991536717
 H,0,2.3098111851,-2.301218408,-4.5424484259

PCM TS of dichlorovinylketone with thiolate

PCM high precision freq calc for dichlorovinylketone thiolate ts
 B3LYP/6-31+G**

E(RB3LYP) = -1819.74108745

Zero-point correction= 0.187985 (Hartree/Particle)
 Thermal correction to Energy= 0.204422
 Thermal correction to Enthalpy= 0.205366
 Thermal correction to Gibbs Free Energy= 0.140051
 Sum of electronic and ZPE= -1819.553102
 Sum of electronic and thermal Energies= -1819.536665
 Sum of electronic and thermal Enthalpies= -1819.535721
 Sum of electronic and thermal Free Energies= -1819.601036

E CV S
 KCal/Mol Cal/Mol-K Cal/Mol-K
 Total 128.277 57.588 137.467
 Zero-point correction= 0.187985 (Hartree/Particle)
 Thermal correction to Energy= 0.204422
 Thermal correction to Enthalpy= 0.205366
 Thermal correction to Gibbs Free Energy= 0.140051
 Sum of electronic and ZPE= -1819.553102
 Sum of electronic and thermal Energies= -1819.536665
 Sum of electronic and thermal Enthalpies= -1819.535721
 Sum of electronic and thermal Free Energies= -1819.601036

E CV S
 KCal/Mol Cal/Mol-K Cal/Mol-K
 Total 128.277 57.588 137.467

C	4.00827	-0.32364	-3.84599
C	2.68716	-0.48213	-3.42395
C	2.25059	0.02278	-2.1802
C	3.20488	0.69123	-1.38464
C	4.52484	0.84574	-1.81353
C	4.9567	0.33919	-3.04969
S	0.57216	-0.17711	-1.64034
C	6.39385	0.47797	-3.4964
Cl	0.74225	-3.45465	-1.63076
C	0.26492	-2.26079	-0.38464
Cl	1.57082	-2.08512	0.82219
C	-1.07156	-2.31441	-0.00522
H	2.90131	1.09814	-0.42447
H	5.23161	1.37268	-1.1758
H	4.30717	-0.72045	-4.81409
H	1.97636	-0.9959	-4.06472
H	6.46646	0.58797	-4.58324
H	6.87451	1.34496	-3.03268
H	6.98179	-0.40719	-3.22068
C	-1.76421	-1.64221	1.06262
H	-1.72513	-2.84507	-0.69129
C	-1.06199	-0.69008	2.01569
O	-2.9946	-1.83721	1.21623
H	-1.81821	-0.07337	2.50644
H	-0.51905	-1.25146	2.78413
H	-0.33762	-0.05265	1.50248

Rotational ts 6 via which 2 and 3 interconvert

PCM opt of chlorovinylketone with thiolate attached 2.1A flipped x-coo

B3LYP/6-31+G**

E(RB3LYP) = -1819.74946672

Zero-point correction= 0.187884 (Hartree/Particle)

Thermal correction to Energy= 0.204112

Thermal correction to Enthalpy= 0.205056

Thermal correction to Gibbs Free Energy= 0.141699

Sum of electronic and ZPE= -1819.561582

Sum of electronic and thermal Energies= -1819.545355

Sum of electronic and thermal Enthalpies= -1819.544411

Sum of electronic and thermal Free Energies= -1819.607768

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 128.082	57.735	133.346

C,0,-7.7909186305,0.4428617359,-3.7995773958
 C,0,-6.4793989146,-0.0348728755,-3.9381578489
 C,0,-6.2180443935,-1.3921710616,-3.7016296815
 C,0,-7.2504554499,-2.2491273311,-3.3147836662
 C,0,-8.5645403688,-1.7802674173,-3.1599945788
 C,0,-8.8164576033,-0.4225026798,-3.414998766
 S,0,-5.1759699674,1.0579784753,-4.5222721801
 C,0,-4.3022704134,1.7725091033,-3.0734137176
 Cl,0,-5.6749842947,2.7061423933,-1.9585561106
 C,0,-3.3239729301,2.7546483863,-3.4777188737
 C,0,-1.9471183153,2.6501903263,-3.7628548662
 O,0,-1.2836768103,3.670724567,-4.139777832
 C,0,-1.166759505,1.3401661887,-3.6694464586
 Cl,0,-3.6985134436,0.4251188762,-1.9400446656
 H,0,-0.3344885369,1.3955503985,-4.376428906
 H,0,-0.7451506885,1.2193359612,-2.6647267392
 H,0,-1.7661232227,0.4539291146,-3.8857627965
 H,0,-3.753342722,3.7344195954,-3.6669843831
 H,0,-5.2108137793,-1.7771811939,-3.8231173791
 H,0,-7.0316493737,-3.2990990763,-3.1371572262
 C,0,-9.6726642804,-2.7047468127,-2.7140925778
 H,0,-9.8281958895,-0.037315829,-3.3152601001
 H,0,-8.0069613216,1.4884285229,-3.9936287035
 H,0,-9.7800746826,-2.68477078,-1.6222399409
 H,0,-9.4697457701,-3.7399222049,-3.0036100969
 H,0,-10.6355696924,-2.4088193827,-3.1411445088

Progdyn.conf for PCM trajectories

```

#This is the configuration file for PROGDYN. This file is read by progdynstarterHP and
# the awk programs proggenHP, prog1stpoint, prog2ndpoint, and progdynb.
#The programs won't read anything past the first blank line,
#and this file must end with a blank line.
#The program has a number of default values but they are unlikely to be what you want.
#Do not delete lines - rather, comment out lines for unwanted options.
#The values here are read repeatedly and most can be changed in the middle of running
jobs
****The keywords are case sensitive. The following keywords should always be
defined:****
****method, charge, multiplicity, memory, processors, title
**** method --The following word is copied exactly to the gaussian input file.
method B3LYP/6-31+G**
**** method2 --The options here are restricted, unrestricted, and read. restricted is the
default
#If the method is U..., put unrestricted here and the .com files will have in them
guess=mix.
#If you put read here, the .com files will contain guess=tcheck, which sometimes makes
things faster, sometimes not.
#The use of read requires a specifically defined checkpoint file name using the keyword
checkpoint.
method2 restricted
charge -1
multiplicity 1
processors 4
**** memory --The following "word" is copied exactly to the gaussian input file after
%mem=.
memory 7200mb
**** killcheck and checkpoint -- You can use a specifically defined checkpoint file
name by putting
#the name after the keyword checkpoint. This is necessary if you use the read option
with method2.
#Defined checkpoint names are an unnecessary modest hassle and if you do not want to
bother, use killcheck 1
killcheck 1
#checkpoint dyn20.chk
**** diagnostics -- 0 prints out nothing extra, 1 (default) prints out extra stuff to a
#file "diagnostics", 2 adds more stuff, 3 adds velocities to a file "vellist"
#4 adds the apparent temperature to vellist, but this is meaningless with quasiclassical
calculations

```

```
diagnostics 0
**** title -- the title keyword must be followed by exactly four words
title Dichlorovinylketone classical trajectories 298.15
**** initialdis -- 0 (default) turns off displacement of the normal modes, so that all
trajectories start from the same place
# and only the energies and signs of the motion in the modes are randomized
# 1 gives a flat distribution of displacements where all of the possible values are equally
likely
# 2 (recommended) gives a QM-like gaussian distribution of displacements, so that
displacements in the middle are more likely than
# those at the end by 1/e
initialdis 0
**** timestep -- this is the time between points in the trajectory. Typical values would
be 1E-15 or 0.5E-15 or 0.25E-15
timestep 1E-15
**** scaling -- this lets you scale the gaussian frequencies by a constant
scaling 1.0
temperature 298.15
**** method3, method4, method5, and method6 -- These keywords let you add extra
lines to the gaussian input file.
#method3 and method4 add lines at the top of the input after the lines defining the
method, and
#this is useful to implement things like the iop for mPW1k
#method5 and method6 add lines after the geometry, after a blank line of course
#only a single term with no spaces can be added, one per method line. Here are some
examples to uncomment if needed
#method3 IOp(3/76=0572004280)
#method3 scrf=(pcm,solvent=ethanol)
#add the line below with big structures to get it to put out the distance matrix and the
input orientation
#method3 iop(2/9=2000)
method4 scrf=(pcm,solvent=ethanol)
#method5 radii=bondi
#method6
**** methodfile -- This keyword lets you add more complicated endings to gaussian
input files
#such as a gen basis set. Put after the keyword the number of lines in a file you create
called
#methodfile that contains the test you want to add to the end of the gaussian input
methodfile 0
**** numimag --This tells the program the number of imaginary frequencies in the
starting structure.
#if 0, treats as ground state and direction of all modes is random
```



```
#if 1, motion along the reaction coordinate will start out in the direction defined by
searchdir
#if 2, only lowest freq will go direction of searchdir and other imag mode will go in
random direction
numimag 0
**** searchdir -- This keyword says what direction to follow the mode associated with
the imaginary frequency.
#The choices are "negative" and "positive". Positive moves in the direction defined in
the gaussian frequency calculation
#for the imaginary frequency, while negative moves in the opposite direction. The
correct choice can be made either
#by a careful inspection of the normal modes and standard orientation geometry, or by
trial and error.
searchdir positive
**** classical -- for quassiclassical dynamics, the default, use 0. for classical dynamics,
use 1
#if there are no normal modes and the velocities are to be generated from scratch, use
classical 2
classical 0
**** DRP, saddlepoint, and maxAtomMove --to run a DRP use 'DRP 1' in the line
below, otherwise leave it at 0 or comment it out
#the treatment of starting saddlepoints is not yet implemented so use saddlepoint no
#if DRP shows oscillations then decrease maxAtomMove
DRP 0
saddlepoint no
maxAtomMove 0.01
**** cannonball -- The program can "fire" a trajectory from a starting position toward a
particular target, such as toward
#a ts. To use this, make a file cannontraj with numAtom lines and three numbers per
line that defines the vector
#for firing the trajectory, relative to the starting geometry's standard orientation. The
number following cannonball sets
#the extra energy being put into the structure in kcal/mol
#cannonball 10
**** keepevery --This tells the program how often to write the gaussian output file to
file dyn, after the first two points.
#Use 1 for most dynamics to start with, but use a higher number to save on disk space or
molden loading time.
keepevery 1
**** highlevel --For ONIOM jobs, the following line states the number of highlevel
atoms,
#which must come before the medium level atoms. Use some high value such as 999 if
not using ONIOM
highlevel 999
```

```

**** fixedatom1, fixedatom2, fixedatom3, and fixedatom4 - These fix atoms in space.
#Fixing one atom serves no useful purpose and messes things up, while fixing two atoms
#fixes one distance and fixing three has the effect of fixing three distances, not just two
#in current form fixed atoms only are meant to work with no displacements, that is,
initialdis=0
#fixedatom1 2
#fixedatom2 3
#fixedatom3 19
**** boxon and boxsize - With boxon 1, a cubic box is set such that atoms that reach the
edge
#are reflected back toward the middle. Useful for dynamics with solvent molecules.
This is a crude
#implementation that is ok for a few thousand femtoseconds but will not conserve
energy long term.
#Set the box size so as to fit the entire initial molecule but not have too much extra
room.
#The dimensions of the box are two times the boxsize, e.g. boxsize 7.5 leads to a box
that is 15 x 15 x 15 angstroms
#boxon 0
#boxsize 7.5
**** displacements -- This keyword lets you set the initialdis of particular modes by
using a series of lines of the format
# displacements NumberOfMode InitialDisForThatMode, as in the example below. You
should be able to do as many of these as you like
# you might consider this for rotations where a straight-line displacement goes wrong at
large displacements
# The choices for InitialDisForThatMode are 0, 1, 2, and 10, where 10 does the same
thing as 0 but is maintained for now because
# a previous version of the program had a bug that made 0 not work.
#displacements 1 10
**** etolerance --This sets the allowable difference between the desired energy in a
trajectory and the actual
#energy, known after point 1 from the potential energy + the kinetic energy in the initial
velocities.
#The unit is kcal/mol and 1 is a normal value for mid-sized organic systems. For very
large and floppy molecules, a larger value
#may be needed, but the value must stay way below the average thermal energy in the
molecule (not counting zpe).
#If initialdis is not 0 and few trajectories are being rejected, decrease the value.
etolerance 1
**** controlphase --It is sometimes useful to set the phase of particular modes in the
initialization of trajectories.
#The format is controlphase numberOfModeToControl positive or controlphase
numberOfModeToControl negative.

```

```

**** damping -- The damping keyword lets you add or subtract energy from the system
at each point, by multiplying the velocities
#by the damping factor. A damping of 1 has no effect, and since you mostly want to
change the energy slowly, normal values range
#from 0.95 to 1.05. The use of damping lets one do simulated annealing - you add
energy until the structure is moving enough
#to sample the kinds of possibilities you are interested in, then you take away the energy
slowly.
damping 1
**** reversetraj --This keyword sets the trajectories so that both directions from a
transition state are explored.
#reversetraj true

```

```

#updated Aug 9, 2007 to include the possibility of classical dynamics by the keyword
classical
#updated Jan 2008 to include fixed atoms, ONIOM jobs, keepevery, and box size
#update Feb 2008 to include methodfile parameter
# updated Nov 2008 to allow for start without an initial freq calc using classical = 2
# update Aug 2010 to include etolerance, damping controlphase and reversetraj

```

Proganal for PCM trajectories

```

BEGIN {
getline < "isomernumber"
isomer=$1
}
/Dichlorovinylketone/ {
printf("%s %s %s %s %s %s ",$1,$2,$3,$4,$6,$8)
runpoint=$6
}
/Standard orientation/,/Rotational constants/ {
if (($1>.5) && ($1<27)) {
A[$1]=$4;B[$1]=$5;C[$1]=$6
}
}
END {
C10C11=Distance(10,11)
C19C10=Distance(9,10)
S7C10=Distance(7,10)
printf("%s %.3f %s %.3f %s %.3f
","C10C11",C10C11,"C19C10",C19C10,"S7C10",S7C10)

```

```

if (runpoint>500) {
  print "Too many points. XXXXMT"
  movedyn(isomer)
  movetraj(isomer)
}
if (C19C10>2.1) {
  print "Inversion Product XXXX"
  movedyn(isomer)
  movetraj(isomer)
}
if (C10C11>2.1) {
  print "Retention Product XXXX"
  movedyn(isomer)
  movetraj(isomer)
}
if (S7C10>3.5) {
  print "Floated off XXXX"
  movedyn(isomer)
}

system("date '+%b:%d:%Y %T'")
system("tail -1 Echeck | grep XXXX")
}

function Distance(Atom1,Atom2) {
  return sqrt((A[Atom1]-A[Atom2])^2 + (B[Atom1]-B[Atom2])^2 + (C[Atom1]-
C[Atom2])^2)
}

function Angle(Atom1,Atom2,Atom3) {
  value=((-
Distance(Atom1,Atom3)^2+Distance(Atom1,Atom2)^2+Distance(Atom2,Atom3)^2)/(2
*Distance(Atom1,Atom2)*Distance(Atom2,Atom3)))
  return acos(value)
}

function asin(x) { return (180/3.141592)*atan2(x, sqrt(1-x*x)) }

function acos(x) { return (180/3.141592)*atan2(sqrt(1-x*x), x) }

function atan(x) { return (180/3.141592)*atan2(x,1) }

function Dihedral(Atom1,Atom2,Atom3,Atom4) {
  B1x=A[Atom2]-A[Atom1]

```

```

B1y=B[Atom2]-B[Atom1]
B1z=C[Atom2]-C[Atom1]
B2x=A[Atom3]-A[Atom2]
B2y=B[Atom3]-B[Atom2]
B2z=C[Atom3]-C[Atom2]
B3x=A[Atom4]-A[Atom3]
B3y=B[Atom4]-B[Atom3]
B3z=C[Atom4]-C[Atom3]
modB2=sqrt((B2x^2)+(B2y^2)+(B2z^2))
# yAx is x-coord. etc of modulus of B2 times B1
yAx=modB2*(B1x)
yAy=modB2*(B1y)
yAz=modB2*(B1z)
# CP2 is the crossproduct of B2 and B3
CP2x=(B2y*B3z)-(B2z*B3y)
CP2y=(B2z*B3x)-(B2x*B3z)
CP2z=(B2x*B3y)-(B2y*B3x)
termY=((yAx*CP2x)+(yAy*CP2y)+(yAz*CP2z))
# CP is the crossproduct of B1 and B2
CPx=(B1y*B2z)-(B1z*B2y)
CPy=(B1z*B2x)-(B1x*B2z)
CPz=(B1x*B2y)-(B1y*B2x)
termX=((CPx*CP2x)+(CPy*CP2y)+(CPz*CP2z))
dihed4=(180/3.141592)*atan2(termY,termX)
return dihed4
}

function killdyn(isomer) {
  system("rm -f dyn")
}

```

Mechanism of the Fujiwara Hydroarylation

TS 1 Becke/6-31G on C H O F, Lanl2dz on Pd

ts1

TS for EAS of Ringclosure

B3LYP/gen

E(RB+HF-LYP) = -1945.94420951

Zero-point correction= 0.290055 (Hartree/Particle)

Thermal correction to Energy= 0.321600

Thermal correction to Enthalpy= 0.322544

Thermal correction to Gibbs Free Energy= 0.218016

Sum of electronic and ZPE= -1945.654155
 Sum of electronic and thermal Energies= -1945.622610
 Sum of electronic and thermal Enthalpies= -1945.621666
 Sum of electronic and thermal Free Energies= -1945.726193

E CV S
 KCal/Mol Cal/Mol-K Cal/Mol-K
 Total 201.807 111.516 219.996

C,0,0.0728893158,-0.2783031639,1.6318503042
 C,0,-0.5705346032,-0.0580124136,2.8680783866
 C,0,0.1932090128,0.2784958289,4.006354056
 C,0,1.5822290626,0.3847537495,3.901397317
 C,0,2.216235426,0.1692349035,2.6716676445
 C,0,1.4602915388,-0.1668712017,1.5392460062
 C,0,-2.0136318348,-0.2022738723,2.9931742107
 Pd,0,-2.0983607484,-2.6965540421,4.3538836525
 O,0,-3.6885429412,-5.2640224912,3.7471975548
 C,0,-3.2727417637,-4.7275598651,2.7124050827
 C,0,-3.5544845839,-5.3218174184,1.3267157412
 F,0,-2.3749608852,-5.6611560759,0.6734300634
 C,0,-2.8749924021,-1.0434406981,3.517989044
 C,0,-4.337069361,-0.9153684209,3.5247413246
 O,0,-5.190160739,-1.7622180965,3.6660786795
 O,0,-4.8044223246,0.472710252,3.3882055086
 C,0,-3.923791871,1.4698540706,3.0747951189
 C,0,-2.9615963767,1.2334348567,2.0383779333
 C,0,-2.0836977826,2.3207442299,1.6917564442
 C,0,-2.1174472104,3.4920228126,2.4126464034
 C,0,-3.0507844037,3.6543979987,3.4699657905
 C,0,-3.9607912389,2.6586272899,3.8299909574
 C,0,-4.9468734994,2.8194588252,4.9573483506
 O,0,-2.5521903339,-3.6214437499,2.6100498397
 F,0,-4.3307048843,-6.4571219156,1.4041863559
 F,0,-4.2230041761,-4.4091664317,0.5150760671
 H,0,-1.3887957078,2.1920309731,0.8707131198
 H,0,-1.446023091,4.3071821416,2.168902745
 H,0,-3.0566103538,4.5866703556,4.0261749292
 H,0,-0.2998075481,0.405940836,4.9627583493
 H,0,2.1676875022,0.6249033995,4.7821602696
 H,0,3.2954100496,0.2509820281,2.5965843821
 H,0,1.9534318595,-0.3553463348,0.5918136191
 H,0,-0.5116150978,-0.5668799344,0.76421172
 H,0,-5.9753186285,2.6826389584,4.6069378984

H,0,-4.7781994341,2.0687508679,5.7379547238
 H,0,-4.8624258532,3.8107621725,5.4095476609
 H,0,-3.2507134401,0.5579653419,1.2348093676
 O,0,-0.8726928328,-3.9345132351,6.0191063655
 O,0,-1.4354315156,-1.7593629633,6.1170612534
 C,0,-0.8639604791,-2.8213202467,6.6216444814
 C,0,-0.1642733789,-2.6354344725,7.9577397243
 F,0,0.885911717,-1.7306376486,7.8241798345
 F,0,-1.0335222972,-2.1211605616,8.9067297159
 F,0,0.3513371378,-3.815079638,8.4402770022

TS 2 Becke/6-31G* on C H O F, Lan12dz on Pd

ts16-31G*

TS for EAS of Ringclosure

B3LYP/gen

E(RB+HF-LYP) = -1946.41332971

Zero-point correction= 0.290672 (Hartree/Particle)

Thermal correction to Energy= 0.321227

Thermal correction to Enthalpy= 0.322172

Thermal correction to Gibbs Free Energy= 0.220377

Sum of electronic and ZPE= -1946.122658

Sum of electronic and thermal Energies= -1946.092102

Sum of electronic and thermal Enthalpies= -1946.091158

Sum of electronic and thermal Free Energies= -1946.192953

E CV S

KCal/Mol Cal/Mol-K Cal/Mol-K

Total 201.573 109.246 214.245

C,0,0.1134358477,-0.3587725425,1.66486693
 C,0,-0.5568120576,-0.0747088219,2.8681206731
 C,0,0.1803868366,0.2753862422,4.0138860965
 C,0,1.5718298889,0.3303550278,3.9508967662
 C,0,2.2337463543,0.0488164552,2.7535788274
 C,0,1.5031871455,-0.3002278108,1.6128954083
 C,0,-2.0089448885,-0.1624885912,2.9530537889
 Pd,0,-2.2359904791,-2.6086977113,4.3868461569
 O,0,-3.8966627186,-5.0142474983,3.7764354219
 C,0,-3.3390026701,-4.6071530693,2.7743964261
 C,0,-3.5176262634,-5.3291061375,1.4139185154
 F,0,-2.3290096804,-5.7365800068,0.9222119904
 C,0,-2.9076486552,-0.9543923079,3.479291052

C,0,-4.3674506631,-0.7267395833,3.4316322182
 O,0,-5.2555040619,-1.5136202001,3.5292622652
 O,0,-4.7254187546,0.6577413464,3.3019780463
 C,0,-3.786829767,1.5641115793,2.9838604172
 C,0,-2.8648407217,1.260847536,1.9322517697
 C,0,-1.9332599112,2.2866613876,1.5501754235
 C,0,-1.8657249585,3.4542060135,2.2657290547
 C,0,-2.7517383656,3.6766279389,3.3496919618
 C,0,-3.715798613,2.7524053621,3.7377698977
 C,0,-4.6554928661,2.9798671503,4.8927731969
 O,0,-2.5528810352,-3.5772468135,2.6447331878
 F,0,-4.308680539,-6.4016163158,1.5293240737
 F,0,-4.0724261122,-4.4970421398,0.5035390466
 H,0,-1.2738198281,2.109465342,0.7074703694
 H,0,-1.1494826157,4.2247443223,1.998928669
 H,0,-2.6751152455,4.6080129286,3.9052484487
 H,0,-0.3393313829,0.4612857719,4.9478899019
 H,0,2.1385889487,0.5854486982,4.8415064277
 H,0,3.3183221561,0.0910754954,2.7101374346
 H,0,2.0181132036,-0.5388398322,0.6869482945
 H,0,-0.4558217138,-0.6543599403,0.7881512282
 H,0,-5.7008583048,2.9374778554,4.568617016
 H,0,-4.5294268771,2.2060639129,5.658604956
 H,0,-4.4745590072,3.9545141856,5.3536153023
 H,0,-3.2067484516,0.5862213114,1.150333507
 O,0,-1.2683379142,-3.9225696882,6.00945995
 O,0,-1.6871917683,-1.7562551542,6.22373272
 C,0,-1.2478996339,-2.8698837587,6.6786335052
 C,0,-0.6651844688,-2.8493747142,8.102551389
 F,0,0.4395182137,-2.0739148712,8.1302412191
 F,0,-1.5560272892,-2.3320779456,8.9668727471
 F,0,-0.331121312,-4.0749234085,8.513853302

TS 3 Onsager calc. solvent=ethanol a0=5.63

Onsager ts calculation

B3LYP/gen

E(RB+HF-LYP) = -1946.43659614

Zero-point correction= 0.290830 (Hartree/Particle)

Thermal correction to Energy= 0.322287

Thermal correction to Enthalpy= 0.323231

Thermal correction to Gibbs Free Energy= 0.218656

Sum of electronic and ZPE= -1946.145766

Sum of electronic and thermal Energies= -1946.114309
 Sum of electronic and thermal Enthalpies= -1946.113365
 Sum of electronic and thermal Free Energies= -1946.217940

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	202.238	111.200	220.097
C,0,1.7557254999,-0.5761779355,2.90924804			
C,0,1.837564048,0.0770133023,1.6630013863			
C,0,2.2601522383,1.4201520973,1.6026355007			
C,0,2.590490279,2.095754605,2.7758654365			
C,0,2.5123996272,1.4414975348,4.0075992454			
C,0,2.0864676231,0.1085261241,4.0729676814			
C,0,1.5322685262,-0.6158145109,0.4321241495			
Pd,0,-1.1627551113,0.1868267631,-0.1810918311			
O,0,-3.662032319,-1.2492332657,-1.2056909946			
C,0,-3.0345821011,-1.9184659944,-0.3987074867			
C,0,-3.6150573206,-3.2887310702,0.0473433814			
F,0,-4.2871055425,-3.1516055805,1.2177592721			
C,0,0.6054621017,-0.7104189313,-0.4880696896			
C,0,0.7615228092,-1.44858771,-1.7673586209			
O,0,-0.1048536626,-1.8587005225,-2.4850554059			
O,0,2.0960595908,-1.5996135297,-2.184447031			
C,0,3.1083186137,-1.3554063074,-1.3132299996			
C,0,3.0270186744,-1.9139364446,-0.0029330042			
C,0,4.1539755738,-1.7569474436,0.8663015288			
C,0,5.2223370784,-0.9928296409,0.4664155196			
C,0,5.2284611247,-0.3981034291,-0.8203570779			
C,0,4.1851900912,-0.5545043809,-1.7320687959			
C,0,4.2008938786,0.0676350235,-3.1041883037			
O,0,-1.9337915978,-1.6545699162,0.2226139346			
F,0,-4.4958220102,-3.7648232454,-0.8580176426			
F,0,-2.6726028912,-4.2285974301,0.2280532978			
H,0,4.1469007597,-2.240744233,1.8370467255			
H,0,6.0821254164,-0.8598584611,1.1151617683			
H,0,6.0880562529,0.1995425493,-1.1126898311			
H,0,2.3151651382,1.9204489617,0.6416497148			
H,0,2.9210455565,3.1287519655,2.7271226823			
H,0,2.7903713018,1.9651438702,4.9174613475			
H,0,2.0250964019,-0.3954857145,5.0327451659			
H,0,1.4312767553,-1.611915953,2.9531342911			
H,0,4.136510051,-0.6977003503,-3.8851961429			
H,0,3.3474265843,0.7418564568,-3.2413376485			

H,0,5.11964926,0.6383436628,-3.258829877
 H,0,2.3919459728,-2.7835807938,0.1417451812
 O,0,-2.7184962548,1.8843211161,0.0680977189
 O,0,-0.5835259643,2.1906565403,-0.4594934031
 C,0,-1.7585132966,2.6281740203,-0.230642905
 C,0,-2.0003918406,4.1402453848,-0.388760169
 F,0,-0.8805295895,4.8491304857,-0.2163556813
 F,0,-2.4743266512,4.3938585293,-1.630298642
 F,0,-2.9201576757,4.5718008018,0.4932832137

TS 4 CH Act. TS MPWPW91

CHact-ts

E(RmPW+HF-PW91) = -1419.21440653

Zero-point correction= 0.259659 (Hartree/Particle)

Thermal correction to Energy= 0.282406

Thermal correction to Enthalpy= 0.283350

Thermal correction to Gibbs Free Energy= 0.202832

Sum of electronic and ZPE= -1418.954748

Sum of electronic and thermal Energies= -1418.932000

Sum of electronic and thermal Enthalpies= -1418.931056

Sum of electronic and thermal Free Energies= -1419.011574

E CV S

KCal/Mol Cal/Mol-K Cal/Mol-K

Total 177.213 83.093 169.465

C,0,0.5500941876,0.4217132554,0.0755768144
 C,0,0.7216177488,0.1779628066,1.4299259354
 C,0,1.8929307837,-0.4656570875,1.8235670951
 C,0,2.8877636958,-0.8115826398,0.8893186204
 C,0,2.6726009282,-0.5481060946,-0.4684378194
 C,0,1.5054259331,0.0636566415,-0.8704660022
 C,0,-0.3069633468,0.55662162,2.4473603737
 O,0,1.9988471221,-0.7306868152,3.1477403746
 C,0,3.1910213508,-0.9738270846,3.7999247925
 C,0,4.3295027375,-0.9908147232,2.8921504957
 C,0,4.4896956818,-0.3537839279,1.7655652221
 O,0,3.1724616312,-1.13515711,4.9728029207
 H,0,3.4208365579,-0.8446589818,-1.1880254543

H,0,1.3267316374,0.2544953196,-1.917667804
 H,0,-0.3622530265,0.9014226852,-0.2486557923
 H,0,-1.1412917998,1.0700153694,1.9766070965
 H,0,-0.6895576119,-0.3223678885,2.9635892105
 H,0,0.1156023866,1.2104115053,3.2085040821
 C,0,5.4177899126,0.5587385602,1.1307500651
 C,0,5.0440963939,1.4620608834,0.1387909128
 C,0,5.9825091653,2.3285569842,-0.3913031783
 C,0,7.2951972795,2.2942665432,0.0528589363
 C,0,7.6710704845,1.3984745542,1.0434319125
 C,0,6.7389533236,0.5377071407,1.5883776528
 H,0,4.0204015725,1.4998335014,-0.1965053943
 H,0,5.6861920459,3.0344613355,-1.1523667246
 H,0,8.0253666633,2.9679637178,-0.3702390658
 H,0,8.6919691147,1.3705242656,1.3929048523
 H,0,7.0159217838,-0.1662178807,2.357861609
 Pd,0,4.0555844366,-2.356829007,1.3637391549
 O,0,3.8784608063,-3.9759807185,-0.0763591312
 O,0,5.0609541002,-4.3517719805,1.738722213
 C,0,4.5987025611,-4.7057629473,0.6437845245
 C,0,4.9222236538,-6.097662894,0.1036456926
 F,0,3.8070435353,-6.7353415796,-0.2258534076
 F,0,5.674757101,-5.9913341029,-0.9868391611
 F,0,5.5747064685,-6.8283382254,0.9879843756

O-tolyl-3-phenyl propiolate starting material Becke/6-31G*

Arylprop

lowest energy conf of Aryl propynoate

B3LYP/6-31G*

E(RB+HF-LYP) = -767.326517942

Zero-point correction= 0.233650 (Hartree/Particle)

Thermal correction to Energy= 0.249367

Thermal correction to Enthalpy= 0.250311

Thermal correction to Gibbs Free Energy= 0.186839

Sum of electronic and ZPE= -767.092868

Sum of electronic and thermal Energies= -767.077151

Sum of electronic and thermal Enthalpies= -767.076207

Sum of electronic and thermal Free Energies= -767.139679

E CV S

KCal/Mol Cal/Mol-K Cal/Mol-K

Total 156.480 58.980 133.589

C,0,0.3832022285,-0.1001583836,-0.0700186283
 C,0,0.7967875351,-0.6533159543,1.1395642033
 C,0,2.1623650203,-0.7932413571,1.3882327786
 C,0,3.0920696168,-0.3881324469,0.4309647422
 C,0,2.6527530122,0.1569234117,-0.7761979593
 C,0,1.2905029147,0.3151366923,-1.054546845
 H,0,0.0630186283,-0.9601398127,1.8743923612
 H,0,2.493263513,-1.2201034935,2.3307422786
 H,0,4.156250186,-0.4966131357,0.6208943695
 H,0,3.3776782425,0.4693322598,-1.5240592254
 C,0,0.8076256735,0.9019571362,-2.357809513
 O,0,-0.9711019301,-0.0071389974,-0.417325809
 C,0,-1.8838185426,0.5183269203,0.4553900979
 O,0,-1.6349002638,0.9404094289,1.5617072763
 C,0,-3.1950710374,0.4978045739,-0.1392642907
 C,0,-4.3274208302,0.5144964953,-0.5778981506
 C,0,-5.6529862501,0.5271837978,-1.0992689654
 C,0,-6.7158883509,1.0360202486,-0.3270722494
 C,0,-8.0095132317,1.0453344493,-0.8404325656
 C,0,-8.2601625573,0.5505232836,-2.1230559631
 C,0,-7.2115359969,0.0441365516,-2.8955991758
 C,0,-5.9144073948,0.0305083988,-2.3915285828
 H,0,-6.5118454361,1.4181419108,0.6681515019
 H,0,-8.8243774982,1.4389651713,-0.2395000017
 H,0,-9.2714966724,0.5595105191,-2.5201114861
 H,0,-7.4060236687,-0.3407922278,-3.8926517341
 H,0,-5.0939176765,-0.36119119,-2.9844667483
 H,0,0.2093436247,1.8060331918,-2.1940872605
 H,0,1.653585793,1.1656707605,-2.9994175898
 H,0,0.1696083491,0.1971367975,-2.9033548657

O-tolyl-3-phenyl Propiolate Starting Material Becke/6-31G* (5D in jobfile)

Arylprop2

lowest energy conf of Aryl propynoate

B3LYP/6-31G*

E(RB+HF-LYP) = -767.311245519

Zero-point correction= 0.233779 (Hartree/Particle)

Thermal correction to Energy= 0.249479

Thermal correction to Enthalpy= 0.250423

Thermal correction to Gibbs Free Energy= 0.187025

Sum of electronic and ZPE= -767.077467

Sum of electronic and thermal Energies= -767.061766

Sum of electronic and thermal Enthalpies= -767.060822

Sum of electronic and thermal Free Energies= -767.124221

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 156.551	58.932	133.433

C,0,0.384794033,-0.0901674203,-0.0680655129
C,0,0.8023007369,-0.6318129339,1.145927574
C,0,2.1690233455,-0.7709718074,1.390965575
C,0,3.0963897119,-0.3757230846,0.4269394374
C,0,2.6534991603,0.1583209839,-0.7842225397
C,0,1.290201773,0.3150043967,-1.0593768888
H,0,0.0714855121,-0.9308529488,1.8866125785
H,0,2.5024808707,-1.1892091572,2.3364342967
H,0,4.1610388611,-0.483431532,0.6146117472
H,0,3.3760723296,0.4631752388,-1.537428082
C,0,0.8036761955,0.8894743062,-2.3670533397
O,0,-0.9690418913,0.0038298621,-0.4143393023
C,0,-1.8860783664,0.515291609,0.4615038973
O,0,-1.642336277,0.9249129195,1.574042297
C,0,-3.1954475707,0.4976240382,-0.137513853
C,0,-4.328497327,0.5127591423,-0.5746585709
C,0,-5.6538372719,0.5236264192,-1.0966161638
C,0,-6.7203156826,1.0179593122,-0.319285814
C,0,-8.0140770425,1.0253117048,-0.8332449061
C,0,-8.2613858578,0.5428865439,-2.1215856992
C,0,-7.2092318982,0.0509395612,-2.8992757409
C,0,-5.9119468316,0.0393986168,-2.3946688925
H,0,-6.5189409541,1.3904128305,0.6801379018
H,0,-8.831453891,1.4076563818,-0.228460592
H,0,-9.2725823137,0.5502797663,-2.5189925616
H,0,-7.4010729509,-0.3242644382,-3.9005351528
H,0,-5.0889277383,-0.3410178442,-2.9914334052
H,0,0.2032506029,1.7934042869,-2.2101720632
H,0,1.648026317,1.1496397518,-3.0123748026
H,0,0.1665214157,0.1782684945,-2.9054994217

Distinguishing between isotopic perturbation of equilibria and isotope induced desymmetrization

Displacement Method

The d_6 -bromonium cation structure is first optimized and then a high precision frequency calculation is done to ensure that the Cartesian coordinates of the modes are more accurate i.e. to five decimal places and not the usual two decimal places as in a regular frequency calculation. The lowest energy desymmetrizing mode is identified and then “steps” are made along this mode (5 steps in either direction of the standard orientation point. Frequency calculations are then performed for each of the new points that are obtained via stepping along the mode. The E+ZPE is determined for each point, converted to cm^{-1} and the energy of each point is expressed as a value relative to that of the standard orientation. A five-term polynomial is then solved to obtain values for each term and these terms are then input into a fortran program “NUCFUN” in order to generate the wavefunction. From the wavefunction, the time-averaged geometry of the bromonium cation can be determined. An NMR calculation using the GIAO (gauge including atomic orbitals) method is then performed and isotropic shifts and ultimately, the chemical shift of each quaternary carbon and the difference in chemical shift are determined.

Bromonium Cation MPWPW91/6-31+G** OPT/FREQ CALC.

brom-desymm

mpw1pw91 opt/freq calc of d6-bromonium ion

mPW1PW91/6-31+G**

E(RmPW+HF-PW91) = -2807.44363253

Zero-point correction= 0.147522 (Hartree/Particle)

Thermal correction to Energy= 0.157898

Thermal correction to Enthalpy= 0.158842

Thermal correction to Gibbs Free Energy= 0.112316
 Sum of electronic and ZPE= -2807.296111
 Sum of electronic and thermal Energies= -2807.285734
 Sum of electronic and thermal Enthalpies= -2807.284790
 Sum of electronic and thermal Free Energies= -2807.331317

E CV S
 KCal/Mol Cal/Mol-K Cal/Mol-K
 Total 99.083 37.857 97.924

C,0,-0.0722812533,0.0357154686,0.0488256313
 C,0,0.3496513817,0.4037679942,1.4201951925
 C,0,1.2705230699,-0.4838758456,2.2014249566
 Br,0,-1.6060200852,-0.388134505,1.4340366776
 C,0,0.3296744787,1.8337628835,1.8685125333
 C,0,0.4129820521,-1.2322775257,-0.5862770963
 C,0,-0.52720624,1.0857018857,-0.9191725904
 H,0,-1.0322284067,1.932243531,-0.460995087
 H,0,0.3659756751,1.456870899,-1.4369736714
 H,0,-1.1837877732,0.6469590137,-1.6707727111
 H,0,-0.2888196204,-1.5633106442,-1.3520455863
 H,0,1.3620511744,-1.0010954625,-1.0857614481
 H,0,0.5844731106,-2.0483733261,0.1109640938
 H,0,0.236511299,1.8879640131,2.9533698537
 H,0,1.2989049175,2.2709598368,1.5980868113
 H,0,-0.4541921298,2.4364156901,1.4169143137
 H,0,1.1323561825,-0.3231813661,3.2708386829
 H,0,1.1629177236,-1.5442236983,1.9877506777
 H,0,2.2963094437,-0.1848398419,1.9524397661

Standard Orientation Geometry

C	-0.70366	0.74154	0.00018
C	-0.70589	-0.73972	0.00027
C	-0.97000	-1.50427	1.26199
Br	1.27078	-0.00169	-0.00042
C	-0.97093	-1.50408	-1.26139
C	-0.96552	1.50683	1.26209
C	-0.96714	1.50674	-1.26136
H	-0.62032	1.01549	-2.16690
H	-2.05335	1.64112	-1.33715
H	-0.51710	2.49794	-1.20245
H	-0.51374	2.49726	1.20334
H	-2.05148	1.64312	1.33813

H	-0.61933	1.01478	2.16740
H	-0.52248	-2.49605	-1.20303
H	-2.05738	-1.63679	-1.33685
H	-0.62366	-1.01302	-2.16685
H	-0.52007	-2.49560	1.20373
H	-0.62342	-1.01280	2.16748
H	-2.05624	-1.63861	1.33735

Lowest energy desymmetrizing mode (5th mode)

X	Y	Z
0.10933	-0.06743	-0.00013
-0.12085	-0.0733	0.00009
-0.09699	-0.09504	-0.02132
-0.01323	0.07775	0.0004
-0.09753	-0.09346	0.02065
0.15482	-0.0318	0.00375
0.1513	-0.03413	-0.00482
0.09678	-0.07022	-0.00689
0.17413	0.11934	-0.00175
0.30097	-0.10133	-0.0079
0.31928	-0.10579	0.01016
0.17958	0.13824	-0.00584
0.08768	-0.07368	0.0074
0.09305	-0.01312	-0.05209
-0.08359	-0.31827	0.1797
-0.33636	-0.00715	-0.02155
0.09421	-0.01402	0.05
-0.33594	-0.01005	0.02145
-0.08255	-0.32084	-0.18034

Displacements Method using M06/6-31+G**

m06-freq-0.0025-nmrcalc

M06 freq-nmr calc of d6-bromonium Factor=-0.0025

M06/6-31+G**

E(RM06) = -2806.98253172

Zero-point correction= 0.145344 (Hartree/Particle)

Thermal correction to Energy= 0.155909

Thermal correction to Enthalpy= 0.156853

Thermal correction to Gibbs Free Energy= 0.109785

Sum of electronic and ZPE= -2806.837188

Sum of electronic and thermal Energies= -2806.826623

Sum of electronic and thermal Enthalpies= -2806.825679

Sum of electronic and thermal Free Energies= -2806.872747

E CV S
 KCal/Mol Cal/Mol-K Cal/Mol-K
 Total 97.834 38.376 99.063

6 -0.754042 -0.693531 0.000481
 6 -0.662337 0.777275 0.000401
 6 -0.873711 1.557145 -1.257199
 35 1.267340 -0.074831 -0.000579
 6 -0.871625 1.557538 1.258081
 6 -1.057221 -1.443082 -1.256419
 6 -1.055883 -1.443787 1.257221
 1 -0.678987 -0.978644 2.168321
 1 -2.149785 -1.520799 1.338021
 1 -0.661419 -2.461460 1.193681
 1 -0.665088 -2.461641 -1.192939
 1 -2.151293 -1.517425 -1.337639
 1 -0.679007 -0.978644 -2.167339
 1 -0.349790 2.516495 1.199881
 1 -1.946810 1.773886 1.335381
 1 -0.560412 1.044780 2.168561
 1 -0.355517 2.518020 -1.198299
 1 -0.560165 1.045893 -2.167709
 1 -1.949718 1.769283 -1.335039

NUCFUN

PROGRAM NUCFUN

IMPLICIT REAL*8 (A-H, O-Z)

PARAMETER (MAXPT = 2000, MAXPT2 = 2*MAXPT)

PARAMETER (PI=3.1415927,H=6.62608D-34,C=2.99792458E8)

PARAMETER (AMU=1.66054E-27)

DIMENSION WORK(MAXPT2), PHI(MAXPT)

EXTERNAL VFUNC

COMMON /VFUNCD/ XK, REQUIL, ALPHA, X5, X4, X3, X2, X1

NDP = 0

DPN = NDP

```

C ** RM IS IN ATOMIC MASS UNITS
C ** W IS IN CM-1
C ** XK=DSUBE IS IN CM-1

      RM = 2.1248
C ** removed because I don't think we need them
C   W=214.502
C   XK=12547.

C ** Here are the constants we need for our function
      X5=-226.1655
      X4=227484.27
      X3=-416.3365
      X2=24775.746
      X1=26.109461

C ** ANHARMONICITY CONSTANT IN CM-1
C ** ALPHA IS IN ANGSTROMS-1

C   WX=(W**2)/(4*XK)
C   CONST= 2*(PI**2)*AMU*C/(100*H)
C   ALPHA=(W/1.0D8)*SQRT(CONST*RM/XK)

C ** REDUCED MASS DIVIDED BY HBAR**2
C ** EQUILIBRIUM DISTANCE IN ANGSTROMS

      RM=(RM*AMU*4.0D0*(PI**2)*C/H)*(1.0D-18)
C   REQUIL = 0.0

      RSTART = -0.30
      REND = 0.30
      NPTS = 2001
      TOLER = 1.0D-8
      MAXPASS = 50

C   EIN = W*(DPN+0.5) - WX*((DPN+0.5)**2)

C   EIN = EIN*1.05

      EIN = 200.

      CALL NUMROV(EIN, RSTART, REND, NPTS, RM, VFUNC, TOLER,
MAXPASS,
      $      PHI, EOUT, IPASS, IERR, WORK)

```

```

WRITE (6, '(5X, "EIN = ", D15.8, " EOUT =", D15.8, '//
$   "' IPASS =", I5, " IERR =", I5)') EIN, EOUT, IPASS, IERR
IF (NPTS.NE.0) THEN
  WRITE (6, '(/, "The potential"')
  DO 50 I=1,NPTS,10
    R=RSTART+(I-1)*(REND-RSTART)/(NPTS-1)
    VZ = X5*R**5 + X4*R**4 + X3*R**3 + X2*R**2 +X1*R
C   VZ = XK*( 1 - EXP(-ALPHA*(R-REQUIL)) )**2
    WRITE (6, '(1X, 2F15.4)') R,VZ
50  CONTINUE
  WRITE (6, '(/, "The wave function"')
  DO 60 I=1,NPTS,10
    R=RSTART+(I-1)*(REND-RSTART)/(NPTS-1)
    VZ = X5*R**5 + X4*R**4 + X3*R**3 + X2*R**2 +X1*R
C   VZ = XK*( 1 - EXP(-ALPHA*(R-REQUIL)) )**2
    WRITE (6, '(1X,2F15.4)') R, PHI(I)
60  CONTINUE
  END IF

  STOP

  END
  REAL*8 FUNCTION VFUNC(R)

  IMPLICIT REAL*8 (A-H, O-Z)

C   COMMON /VFUNCD/ XK, REQUIL, ALPHA
  COMMON /VFUNCD/ XK, REQUIL, ALPHA, X5, X4, X3, X2, X1

  VFUNC = X5*R**5 + X4*R**4 + X3*R**3 + X2*R**2 +X1*R
C   VFUNC = XK*( 1 - EXP(-ALPHA*(R-REQUIL)) )**2

  RETURN

  END
  SUBROUTINE NUMROV(EIN, RSTART, REND, NPTS, RM, VFUNC,
$   TOLER, MAXPASS, PHI, EOUT, IPASS, IERR, WORK)
C **
C ** EIN   - (INPUT) INITIAL GUESS OF ENERGY LEVEL
C ** RSTART - (INPUT) STARTING R
C ** REND  - (INPUT) ENDING R
C ** NPTS  - (INPUT) NUMBER OF POINTS TO USE IN GRID (MUST BE
  ODD)

```

```

C ** RM    - (INPUT) REDUCED MASS DIVIDED BY H BAR SQUARED
C ** VFUNC  - (INPUT) EXTERNAL FUNCTION WHICH GIVES POTENTIAL
ENERGY
C ** TOLER  - (INPUT) CONVERGENCE TOLERANCE ON ENERGY
C ** MAXPASS - (INPUT) MAXIMUM NUMBER OF ITERATIONS
C ** PHI    - (OUTPUT) WAVE FUNCTION - MINIMUM DIMENSION NPTS
C ** EOUT   - (OUTPUT) ENERGY LEVEL
C ** IPASS  - (OUTPUT) NUMBER OF ITERATIONS NEEDED
C ** IERR   - (OUTPUT) = 0 CONVERGENCE ACHIEVED
C **       = 1 TOO MANY ITERATIONS NEEDED
C **       = 2 NPTS NOT ODD
C **       = 3 NPTS .LT. 3
C **       = 4 REND .LE. RSTART
C ** WORK   - (SCRATCH) WORK ARRAY - MINIMUM DIMENSION NPTS*2
C **

```

```

IMPLICIT REAL*8(A-H, O-Z)

```

```

EXTERNAL VFUNC
DIMENSION PHI(*), WORK(*)

```

```

C **
C ** IN WORK WE WILL PUT THE F AND PHIR ARRAYS
C **

```

```

IOFF = 0
IOFPHIR = IOFF+NPTS

```

```

IERR = 0
IF (MOD(NPTS, 2) .NE. 1) THEN
  IERR = 2
  RETURN
ELSE IF (NPTS .LT. 3) THEN
  IERR = 3
  RETURN
ELSE IF (REND .LE. RSTART) THEN
  IERR = 4
  RETURN
END IF

```

```

H = (REND-RSTART)/DFLOAT(NPTS-1)

```

```

E = EIN
IPASS = 0

```

```

H2 = H*H/12.0D0
H210 = H2*10.0D0

5 CONTINUE
IPASS = IPASS+1
IF (IPASS .GT. MAXPASS) THEN
  IERR = 1
  RETURN
END IF

DO 10 I = 1, NPTS
  WORK(IOFF+I) = -2.0D0*RM*(E-VFUNC(RSTART+(I-1)*H))
10 CONTINUE
  MIN = 0
  EMIN = 1.0D36
  DO 11 I = 1, NPTS
    IF (EMIN .GT. WORK(IOFF+I)) THEN
      EMIN = WORK(IOFF+I)
      MIN = I
    END IF
  11 CONTINUE

  WORK(IOFPHIR+1) = 0.0D0
  WORK(IOFPHIR+2) = (1.0D0-H2*WORK(IOFF+2))
  $      /(2.0D0+H210*WORK(IOFF+1))

  DO 20 I = 3, MIN
    WORK(IOFPHIR+I) = (1.0D0-H2*WORK(IOFF+I))
  $      /((2.0D0+H210*WORK(IOFF+I-1))-
  $      (1.0D0-H2*WORK(IOFF+I-2))*WORK(IOFPHIR+I-1))
  20 CONTINUE

  PHI(MIN) = 1.0D0
  DO 30 I = MIN-1, 1, -1
    PHI(I) = WORK(IOFPHIR+I+1)*PHI(I+1)
  30 CONTINUE

  WORK(IOFPHIR+NPTS) = 0.D0
  WORK(IOFPHIR+NPTS-1) = (1.0D0-H2*WORK(IOFF+NPTS-1))
  $      /(2.0D0+H210*WORK(IOFF+NPTS))
  DO 50 I = NPTS-2, MIN, -1
    WORK(IOFPHIR+I) = (1.0D0-H2*WORK(IOFF+I))
  $      /((2.0D0+H210*WORK(IOFF+I+1))-

```

```

$          (1.0D0-H2*WORK(IOFF+I+2))*WORK(IOFPHIR+I+1))
50 CONTINUE

```

```

DO 60 I = MIN+1, NPTS
  PHI(I) = WORK(IOFPHIR+I-1)*PHI(I-1)
60 CONTINUE

```

```

XN = 0.0D0
DO 70 I = 1, NPTS
  XN = XN+PHI(I)**2
70 CONTINUE

```

```

DE = ((2.0D0+H210*WORK(IOFF+MIN))*PHI(MIN)
$  -(1.0D0-H2*WORK(IOFF+MIN-1))*PHI(MIN-1)-
$  (1.0D0-H2*WORK(IOFF+MIN+1))*PHI(MIN+1))/(H*H*XN)
DE = DE/(2.0D0*RM)

```

```

PRINT *, 'E, DE, IPASS', E, DE, IPASS
E = E+DE

```

```

IF (DABS(DE/E) .GT. TOLER) GOTO 5

```

```

EOUT = E

```

```

CALL OVRLP(OV, PHI, PHI, RSTART, REND, NPTS)

```

```

FAC = 1.0D0/DSQRT(OV)

```

```

DO 40 I = 1, NPTS
  PHI(I) = FAC*PHI(I)
40 CONTINUE

```

```

RETURN

```

```

END
SUBROUTINE OVRLP(VAL, F1, F2, RSTART, REND, N)
IMPLICIT REAL*8(A-H, O-Z)

```

```

DIMENSION F1(1), F2(1)

```

```

IF (MOD(N, 2) .NE. 1) STOP 'OVRLP- N NOT ODD'
IF (N .LT. 3) STOP 'N .LT. 3'

```

```

H = (REND-RSTART)/DFLOAT(N-1)

```

```

H13 = H/3.0D0
H43 = 4.0D0*H13
H23 = 2.0D0*H13
V = 0.D0
DO 10 I = 1, N-2, 2
  V = V+F1(I)*F2(I)*H23+F1(I+1)*F2(I+1)*H43
10 CONTINUE
VAL = V-F1(1)*F2(1)*H13+F1(N)*F2(N)*H13

RETURN

END

```

Hydrogen Phthalate MPW1PW91/6-31+G**

Hydro-phthal-minHP

b3lyp HP freq calc of hydrogen-phthalate

B3LYP/6-31+G**

Zero-point correction= 0.113560 (Hartree/Particle)

Thermal correction to Energy= 0.122987

Thermal correction to Enthalpy= 0.123932

Thermal correction to Gibbs Free Energy= 0.077740

Sum of electronic and ZPE= -608.802179

Sum of electronic and thermal Energies= -608.792752

Sum of electronic and thermal Enthalpies= -608.791808

Sum of electronic and thermal Free Energies= -608.837999

```

E    CV    S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 77.176 35.445 97.219

```

```

6 0.000000 1.376790 -1.444841
6 0.000000 0.712330 -0.202331
6 0.000000 -0.712330 -0.202331
6 0.000000 -1.376790 -1.444841
6 0.000000 -0.698510 -2.658751
6 0.000000 0.698510 -2.658751
6 0.000000 1.683360 1.002629
8 0.000000 2.897880 0.766829
6 0.000000 -1.683360 1.002629
8 0.000000 1.189000 2.197649
1 0.000000 -2.460440 -1.410081
1 0.000000 -1.255060 -3.593471
1 0.000000 1.255060 -3.593471
1 0.000000 2.460440 -1.410081

```

```

8 0.000000 -2.897880 0.766829
8 0.000000 -1.189000 2.197649
1 0.000000 0.000000 2.215019

```

Dynamic Trajectory Method

Dynamic trajectories were initiated from the geometry obtained from a high precision frequency calculation. Each trajectory was allowed to run for 500 fs. A total of 250 trajectories each consisting of 500 points were obtained and the time-averaged geometry of the structure was determined using a program (progaverage3) specifically written to average the geometries of all the points within the trajectories. An NMR calculation was then performed on the time averaged geometry so determined.

Progaverage3-mdfd

```

BEGIN {
count=0
for(i=1;i<=19;i++) {
  x[i]=0;y[i]=0;z[i]=0
}
}

/Input orientation/,/Distance matrix/ {
if ($3==0) {
  if ($2==6) at[$1]="C"
  if ($2==1) at[$1]="H"
  if ($2==35) at[$1]="Br"
  x[$1]=$4;y[$1]=$5;z[$1]=$6
}
if ($1=="Distance") {
  count++
  cc2=cc2+Distance(1,2)
  cc3=cc3+Distance(2,3)
  brc4=brc4+Distance(1,4)
  cc5=cc5+Distance(2,5)
}
}

```


$cc6=cc6+Distance(1,6)$
 $cc7=cc7+Distance(1,7)$
 $hc8=hc8+Distance(8,7)$
 $hc9=hc9+Distance(9,7)$
 $hc10=hc10+Distance(10,7)$
 $hc11=hc11+Distance(11,6)$
 $hc12=hc12+Distance(12,6)$
 $hc13=hc13+Distance(13,6)$
 $hc14=hc14+Distance(14,5)$
 $hc15=hc15+Distance(15,5)$
 $hc16=hc16+Distance(16,5)$
 $hc17=hc17+Distance(17,3)$
 $hc18=hc18+Distance(18,3)$
 $hc19=hc19+Distance(19,3)$
 $ccc3=ccc3+Angle(3,2,1)$
 $brcc4=brcc4+Angle(4,1,2)$
 $ccc5=ccc5+Angle(5,2,1)$
 $ccc6=ccc6+Angle(6,1,2)$
 $ccc7=ccc7+Angle(7,1,2)$
 $hcc8=hcc8+Angle(8,7,1)$
 $hcc9=hcc9+Angle(9,7,1)$
 $hcc10=hcc10+Angle(10,7,1)$
 $hcc11=hcc11+Angle(11,6,1)$
 $hcc12=hcc12+Angle(12,6,1)$
 $hcc13=hcc13+Angle(13,6,1)$
 $hcc14=hcc14+Angle(14,5,2)$
 $hcc15=hcc15+Angle(15,5,2)$
 $hcc16=hcc16+Angle(16,5,2)$
 $hcc17=hcc17+Angle(17,3,2)$
 $hcc18=hcc18+Angle(18,3,2)$
 $hcc19=hcc19+Angle(19,3,2)$
 $dih4=dih4+Dihedral(4,1,2,3)$
 $dih5=dih5+Dihedral(5,2,1,4)$
 $dih6=dih6+Dihedral(6,1,2,3)$
 $dih7=dih7+Dihedral(7,1,2,3)$
 if (Dihedral(7,1,2,3)>24) dih7=dih7-360.
 $dih8=dih8+Dihedral(8,7,1,2)$
 if (Dihedral(8,7,1,2)>148) dih8=dih8-360.
 $dih9=dih9+Dihedral(9,7,1,2)$
 if (Dihedral(9,7,1,2)<-92) dih9=dih9+360.
 $dih10=dih10+Dihedral(10,7,1,2)$
 if (Dihedral(10,7,1,2)>25) dih10=dih10-360.
 $dih11=dih11+Dihedral(11,6,1,2)$
 if (Dihedral(11,6,1,2)<-25) dih11=dih11+360.

```

dih12=dih12+Dihedral(12,6,1,2)
if (Dihedral(12,6,1,2)>92) dih12=dih12-360.
dih13=dih13+Dihedral(13,6,1,2)
if (Dihedral(13,6,1,2)<-148) dih13=dih13+360.
dih14=dih14+Dihedral(14,5,2,1)
if (Dihedral(14,5,2,1)<-25) dih14=dih14+360.
dih15=dih15+Dihedral(15,5,2,1)
if (Dihedral(15,5,2,1)>92) dih15=dih15-360
dih16=dih16+Dihedral(16,5,2,1)
if (Dihedral(16,5,2,1)<-148) dih16=dih16+360.
dih17=dih17+Dihedral(17,3,2,1)
if (Dihedral(17,3,2,1)>25) dih17=dih17-360.
dih18=dih18+Dihedral(18,3,2,1)
if (Dihedral(18,3,2,1)>148) dih18=dih18-360.
dih19=dih19+Dihedral(19,3,2,1)
if (Dihedral(19,3,2,1)<-92) dih19=dih19+360.
#other important distances
  BrToC1=BrToC1+Distance(1,4)
  BrToC2=BrToC2+Distance(2,4)
}
}
END {
#print "count",count
print "cc2",cc2/count
print "cc3",cc3/count
print "brc4",brc4/count
print "cc5",cc5/count
print "cc6",cc6/count
print "cc7",cc7/count
print "hc8",hc8/count
print "hc9",hc9/count
print "hc10",hc10/count
print "hc11",hc11/count
print "hc12",hc12/count
print "hc13",hc13/count
print "hc14",hc14/count
print "hc15",hc15/count
print "hc16",hc16/count
print "hc17",hc17/count
print "hc18",hc18/count
print "hc19",hc19/count
print "ccc3",ccc3/count
print "brcc4",brcc4/count
print "ccc5",ccc5/count

```

```
print "ccc6",ccc6/count
print "ccc7",ccc7/count
print "hcc8",hcc8/count
print "hcc9",hcc9/count
print "hcc10",hcc10/count
print "hcc11",hcc11/count
print "hcc12",hcc12/count
print "hcc13",hcc13/count
print "hcc14",hcc14/count
print "hcc15",hcc15/count
print "hcc16",hcc16/count
print "hcc17",hcc17/count
print "hcc18",hcc18/count
print "hcc19",hcc19/count
print "dih4",dih4/count
print "dih5",dih5/count
print "dih6",dih6/count
print "dih7",dih7/count
print "dih8",dih8/count
print "dih9",dih9/count
print "dih10",dih10/count
print "dih11",dih11/count
print "dih12",dih12/count
print "dih13",dih13/count
print "dih14",dih14/count
print "dih15",dih15/count
print "dih16",dih16/count
print "dih17",dih17/count
print "dih18",dih18/count
print "dih19",dih19/count
#test=Dihedral(4,1,2,3)
#test=Dihedral(1,2,3,4)
#test=Dihedral(1,2,5,19)
#other important distances
print
print "BrToC1",BrToC1/count
print "BrToC2",BrToC2/count
print "Count",count
}

function Distance(Atom1,Atom2) {
  return sqrt((x[Atom1]-x[Atom2])^2 + (y[Atom1]-y[Atom2])^2 + (z[Atom1]-
z[Atom2])^2)
}
```

```
function Angle(Atom1,Atom2,Atom3) {
  value=((-
Distance(Atom1,Atom3)^2+Distance(Atom1,Atom2)^2+Distance(Atom2,Atom3)^2)/(2
*Distance(Atom1,Atom2)*Distance(Atom2,Atom3)))
  return acos(value)
}
```

```
function asin(x) { return (180/3.141592)*atan2(x, sqrt(1-x*x)) }
```

```
function acos(x) { return (180/3.141592)*atan2(sqrt(1-x*x), x) }
```

```
function atan(x) { return (180/3.141592)*atan2(x,1) }
```

```
function Dihedral(Atom1,Atom2,Atom3,Atom4) {
# print at[Atom1],x[Atom1],y[Atom1],z[Atom1]
# print at[Atom2],x[Atom2],y[Atom2],z[Atom2]
# print at[Atom3],x[Atom3],y[Atom3],z[Atom3]
# print at[Atom4],x[Atom4],y[Atom4],z[Atom4]
  B1x=x[Atom2]-x[Atom1]
  B1y=y[Atom2]-y[Atom1]
  B1z=z[Atom2]-z[Atom1]
  B2x=x[Atom3]-x[Atom2]
  B2y=y[Atom3]-y[Atom2]
  B2z=z[Atom3]-z[Atom2]
  B3x=x[Atom4]-x[Atom3]
  B3y=y[Atom4]-y[Atom3]
  B3z=z[Atom4]-z[Atom3]
# print "B1",B1x,B1y,B1z
# print "B2",B2x,B2y,B2z
# print "B3",B3x,B3y,B3z
  modB2=sqrt((B2x^2)+(B2y^2)+(B2z^2))
# print "modB2",modB2
# yAx is x-coord. etc of modulus of B2 times B1
  yAx=modB2*(B1x)
  yAy=modB2*(B1y)
  yAz=modB2*(B1z)
# print "yA",yAx,yAy,yAz
# CP2 is the crossproduct of B2 and B3
  CP2x=(B2y*B3z)-(B2z*B3y)
  CP2y=(B2z*B3x)-(B2x*B3z)
  CP2z=(B2x*B3y)-(B2y*B3x)
# print "CP2",CP2x,CP2y,CP2z
  termY=((yAx*CP2x)+(yAy*CP2y)+(yAz*CP2z))
```

```

# print "termY",termY
# CP is the crossproduct of B1 and B2
  CPx=(B1y*B2z)-(B1z*B2y)
  CPy=(B1z*B2x)-(B1x*B2z)
  CPz=(B1x*B2y)-(B1y*B2x)
# print "CP",CPx,CPy,CPz
  termX=((CPx*CP2x)+(CPy*CP2y)+(CPz*CP2z))
# print "termX",termX
# return atan2(termX,termY)
  dihed4=(180/3.141592)*atan2(termY,termX)
# print "dihed4",dihed4
  return dihed4
}

```

PERTURBATION METHOD

For this method anharmonic frequency calculations were ran in Gaussian'09.

Upon completion, the average vibrational geometry at 0 K was obtained and an NMR calculation was performed to determine the chemical shifts of the quaternary carbon in the d6-bromonium cation.

Anharmonic Calculation MPW1PW91/6-31+G**

```

mpw1pw91-anharmlog
mpw1pw91 freq calc of d6-bromonium
mPW1PW91/6-31+G**
E(RmPW+HF-PW91) = -2807.44363249

```

```

Zero-point correction= 0.147523 (Hartree/Particle)
Thermal correction to Energy= 0.157899
Thermal correction to Enthalpy= 0.158843
Thermal correction to Gibbs Free Energy= 0.112318
Sum of electronic and ZPE= -2807.296109
Sum of electronic and thermal Energies= -2807.285733
Sum of electronic and thermal Enthalpies= -2807.284789
Sum of electronic and thermal Free Energies= -2807.331314

```

```

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

```

Total 99.083 37.856 97.920

6 -0.703663 0.741537 0.000182
 6 -0.705891 -0.739725 0.000268
 6 -0.969988 -1.504278 1.261993
 35 1.270784 -0.001681 -0.000424
 6 -0.970926 -1.504081 -1.261393
 6 -0.965527 1.506826 1.262087
 6 -0.967149 1.506735 -1.261364
 1 -0.620326 1.015486 -2.166900
 1 -2.053363 1.641106 -1.337144
 1 -0.517109 2.497942 -1.202451
 1 -0.513750 2.497258 1.203341
 1 -2.051486 1.643110 1.338133
 1 -0.619328 1.014772 2.167402
 1 -0.522470 -2.496056 -1.203029
 1 -2.057375 -1.636802 -1.336847
 1 -0.623656 -1.013022 -2.166845
 1 -0.520060 -2.495605 1.203728
 1 -0.623408 -1.012807 2.167483
 1 -2.056232 -1.638620 1.337350

**Anharmonic Calc. B3LYP/6-31G*--Hydrogen Phthalate—atom10 is
¹⁸O**

hydro-phthal-anharm-atom10-O18
 anharmonic-freq calc of hydro-phthal-atom10 is O18
 B3LYP/6-31G*
 E(RB+HF-LYP) = -608.856465241

Zero-point correction= 0.113435 (Hartree/Particle)
 Thermal correction to Energy= 0.122949
 Thermal correction to Enthalpy= 0.123894
 Thermal correction to Gibbs Free Energy= 0.077781
 Sum of electronic and ZPE= -608.743031
 Sum of electronic and thermal Energies= -608.733516
 Sum of electronic and thermal Enthalpies= -608.732572
 Sum of electronic and thermal Free Energies= -608.778685

E CV S
 KCal/Mol Cal/Mol-K Cal/Mol-K
 Total 77.152 35.722 97.052

C,0,0,-1.4432536102,1.3752619006
 C,0,0,-0.2024393756,0.7112147683

C,0,0.,-0.2024393756,-0.7112147683
 C,0,0.,-1.4432536102,-1.3752619006
 C,0,0.,-2.655866388,-0.6979216838
 C,0,0.,-2.655866388,0.6979216838
 C,0,0.,1.0011954358,1.6838257741
 O,0,0.,0.7616625836,2.8952317201
 C,0,0.,1.0011954358,-1.6838257741
 O,0,0.,2.1964623586,1.1912785529
 H,0,0.,-1.4030352726,-2.4589515822
 H,0,0.,-3.5921277413,-1.2538890651
 H,0,0.,-3.5921277413,1.2538890651
 H,0,0.,-1.4030352726,2.4589515822
 O,0,0.,0.7616625836,-2.8952317201
 O,0,0.,2.1964623586,-1.1912785529
 H,0,0.,2.2051040196,0.

Anharmonic Calc. B3LYP/6-31G*--Hydrogen Phthalate—atom8 is ¹⁸O

hydro-phthal-anharm-atom8-O18
 anharmonic-freq calc of hydro-phthal-atom8 is O18
 B3LYP/6-31G*
 E(RB+HF-LYP) = -608.856465233

Zero-point correction= 0.113444 (Hartree/Particle)
 Thermal correction to Energy= 0.122959
 Thermal correction to Enthalpy= 0.123903
 Thermal correction to Gibbs Free Energy= 0.077783
 Sum of electronic and ZPE= -608.743022
 Sum of electronic and thermal Energies= -608.733507
 Sum of electronic and thermal Enthalpies= -608.732563
 Sum of electronic and thermal Free Energies= -608.778682

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	77.158	35.705	97.066

6	0.000000	1.375262	-1.442553
6	0.000000	0.711215	-0.201738
6	0.000000	-0.711215	-0.201738
6	0.000000	-1.375262	-1.442553
6	0.000000	-0.697922	-2.655165
6	0.000000	0.697922	-2.655165
6	0.000000	1.683826	1.001896

```

8 0.000000 2.895232 0.762364
6 0.000000 -1.683826 1.001896
8 0.000000 1.191279 2.197163
1 0.000000 -2.458952 -1.402334
1 0.000000 -1.253889 -3.591427
1 0.000000 1.253889 -3.591427
1 0.000000 2.458952 -1.402334
8 0.000000 -2.895232 0.762364
8 0.000000 -1.191279 2.197163
1 0.000000 0.000000 2.205805

```

Listing of Dynamics Programs for Program Suite PROGDYN

1. Program progdynstarterHP

```

#!/bin/bash

#progdynstarterHP, made to use high-precision modes from Gaussian output with
#freq=hpmodes
#updated to create a random number file temp811 that is used by proggenHP
#version September 16, 2005, made for workstations
#version August 2007 to allow periodic copying of g09.log to dyn putting it under
#control of progdynb
#version Feb 2008 moves variables like the scratch directory and location of randgen to
#the beginning
#version March 2008 added proganal reporting to points 1 and 2
#version Jan 2009 fixed bug generator of having proganal run twice in checking for
#complete runs
#version May 2009 Echeck catches bad energies after only one point, other lines written
#simpler, triple while loop, revised comments
#version Aug 2010 isomernumber adds words to ease parsing, increased elements up to
#bromine, runpointnumber checked for more appropriate restarts
#
#LIMITATIONS - standard version only handles elements up to bromine, must change
#program to do higher atomic numbers
# only handles up to 4000th excited state for modes - this could start to affect the
#initialization of classical modes or transition vectors at
# extremely high temperatures
# The routine that checks whether the actual energy approximately equals the desired
#energy checks for lines containing "SCF Done" or "EUMP2 =" or " Energy="
# This should handle ordinary calculations HF, DFT, ONIOM, and MP2 calculatons
#but the routine in prog2ndpoint would have to be changed for other calcs.
#

```



```

#                               OUTLINE
# A. initialize to perform Gaussian jobs and know where we are
#  start loop
# B. if no file named "skipstart" then generate a new isomer. Instructions: Get rid of
skipstart to start new isomer.
#  the B loop generates geoPlusVel, adds it to geoRecord, generates and runs first and
second points, and sets up for continuous loop
# C. loop over propagation steps
#
# AAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAA
#origdir, randdir, scratchdir, g09root, logfile all may need varied from system to system
and assigned here or by program calling this one
export LC_ALL=C
export g09root=/usr/local/g09
source $g09root/g09/bsd/g09.profile
origdir=`pwd`
cd $origdir
logfile=xlog
randdir=~/.bin
scratchdir=$1
programdir=~/.a1
freqfile=~/.a1/freqinHP
echo ORIGDIR:
echo $origdir
echo SCRATCHDIR:
echo $scratchdir
echo PROGRAMDIR:
echo $programdir

rm -f nogo # assume that if someone is starting a job, they want it to go.
rm -f diagnostics # contains extra info from start of progFS

#### Triple 'while' loop - will have to break multiple times to get out, but advantage is
ability to control starting over
while (true)
do

# As long as there is a file "goingwell" the program will not exit entirely by itself
rm -f goingwell
while (true)
do
# BBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBB
if (test -f skipstart) then
    echo "skipping start and continuing from previous runs"

```

```

else
#
B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1
generate geoPlusVel and first input file
  if [ `cat runpointnumber` = "1" ]; then
    echo "XXXX did not complete first point so new isomer started" >> dynfollowfile
  fi
  if [ `cat runpointnumber` = "2" ]; then
    echo "XXXX did not complete second point so new isomer started" >>
dynfollowfile
  fi
  if [ `cat runpointnumber` = "3" ]; then
    echo "XXXX did not complete third point so new isomer started" >> dynfollowfile
  fi
  cd $origdir
  $randdir/randgen > temp811
# the next 8 lines would have to be changed to use low-precision modes
  awk '/ 1 2 3 4/,/Harmonic frequencies/ {print}' $freqfile >
temp401
  awk '/Frequencies --/ {print $3;print $4;print $5;print $6;print $7}' temp401 >
tempfreqs
  awk '/Reduced masses/ {print $4;print $5;print $6;print $7;print $8}' temp401 >
tempredmass
  awk '/Force constants/ {print $4;print $5;print $6;print $7;print $8}' temp401 >
tempfrc
  awk '/0/ && ((length($1) < 2) && ($1 < 4)) {print}' temp401 > tempmodes
  awk '/has atomic number/ {print}' $freqfile > tempmasses
  awk '/Standard orientation:./,/tional const/ {if ($3==0) print}' $freqfile >
tempstangeos
  awk -f $programdir/proggenHP $freqfile > geoPlusVel
  if (test -f isomernumber) then
    cp isomernumber temp533
    awk 'BEGIN {getline;i=$1+1;print i,"----trajectory isomer number----"}' temp533
> isomernumber
    rm temp533
  else
    echo "1 ----trajectory isomer number----" > isomernumber
  fi
  echo 1 > runpointnumber
  rm g09.com
  awk -f $programdir/prog1stpoint isomernumber > g09.com
#
B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2
B2B2 if first part successfule then clean up and run the first input file, otherwise die

```



```

grep 'Normal termination' $scratchdir/g09.log > goingwell
if (test -s goingwell) then
  cp $scratchdir/g09.log olddynrun
  cat $scratchdir/g09.log >> dyn
  awk -f $programdir/proganal $scratchdir/g09.log >> dynfollowfile
  awk '/Input orientation/,/Distance matrix/ {print}' olddynrun | awk '/ 0 /
{print}' > old
  awk '/Input orientation/,/Distance matrix/ {print}' olderdynrun | awk '/ 0 /
{print}' > older
  echo 3 > runpointnumber
  awk -f $programdir/progdynb olddynrun > g09.com
  rm -f old older
else
  cp $scratchdir/g09.log $origdir/g09.log
  break
fi
else
  break
fi
# we've just completed a start, so lets skipstart until instructed otherwise
echo "forward" > skipstart
fi
# Reverse trajectories starter routine
if [ `cat skipstart` = "reverserestart" ]; then
  cd $origdir
  rm g09.com
  echo 1 > runpointnumber
  awk -f $programdir/prog1stpoint isomernumber > g09.com
  if (test -s g09.com) then
    rm -f goingwell
    cd $scratchdir
    cp $origdir/g09.com $scratchdir/g09.com
    $g09root/g09/g09 $scratchdir/g09.com > $scratchdir/g09.log
    cd $origdir
    grep 'Normal termination' $scratchdir/g09.log > goingwell
    if (test -s goingwell) then
      cp $scratchdir/g09.log olderdynrun
    else
      cp $scratchdir/g09.log $origdir/g09.log
      break
    fi
  else
    break
  fi
fi

```

```

rm g09.com
echo 2 > runpointnumber
awk -f $programdir/prog2ndpoint $scratchdir/g09.log > g09.com
awk -f $programdir/proganal $scratchdir/g09.log >> dynfollowfile
rm -f tempdone
if (test -s g09.com) then
  rm -f goingwell
  cd $scratchdir
  cp $origdir/g09.com $scratchdir/g09.com
  $g09root/g09/g09 $scratchdir/g09.com > $scratchdir/g09.log
cd $origdir
grep 'Normal termination' $scratchdir/g09.log > goingwell
if (test -s goingwell) then
  cp $scratchdir/g09.log olddynrun
  cat $scratchdir/g09.log >> dyn
  awk -f $programdir/proganal $scratchdir/g09.log >> dynfollowfile
  awk '/Input orientation/,/Distance matrix/ {print}' olddynrun | awk '/ 0 /
{print}' > old
  awk '/Input orientation/,/Distance matrix/ {print}' olderdynrun | awk '/ 0 /
{print}' > older
  echo 3 > runpointnumber
  awk -f $programdir/progdynb olddynrun > g09.com
  rm -f old older
else
  cp $scratchdir/g09.log $origdir/g09.log
  break
fi
else
  break
fi
# we've just completed a reversestart, so lets skipstart until instructed otherwise
echo "reverse" > skipstart
fi

#
END_of_B__END_of_B__END_of_B__END_of_B__END_of_B__END_of_B__
__END_of_B__END_of_B__

#
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCC propagation loop
  while (true)
  do
#increment runpointnumber

```

```

cp runpointnumber temp533
awk 'BEGIN {getline;i=$1+1;print i}' temp533 > runpointnumber
rm temp533
rm -f goingwell
cd $scratchdir
cp $origdir/g09.com $scratchdir/g09.com
$g09root/g09/g09 $scratchdir/g09.com > $scratchdir/g09.log
cd $origdir
grep 'Normal termination' $scratchdir/g09.log > goingwell
if (test -s goingwell) then
  cp olddynrun olderdynrun
  cp $scratchdir/g09.log olddynrun
  awk '/Input orientation/,/Distance matrix/ {print}' olddynrun | awk '/ 0 / {print}'
> old
  awk '/Input orientation/,/Distance matrix/ {print}' olddynrun | awk '/ 0 /
{print}' > older
  awk -f $programdir/progdynb olddynrun > g09.com
  rm -f old older
else
  cp $scratchdir/g09.log $origdir/g09.log
  break
fi

# here is a cool link that lets you interrupt the dynamics with a short job, then
# it automatically goes back to the dynamics just make the file 'detour' and it
# will delete detour, run run.com, then go back to dynamics
if (test -f detour) then
  rm detour
  date >> $logfile
  cat run.com >> $logfile
  cp run.log temp.log
  cd $scratchdir
  $g09root/g09/g09 $origdir/run.com > $origdir/run.log
  cd $origdir
fi

#stop it all nicely by creating a nogo file
if (test -f nogo) then
  break
fi

#figure out if this isomer is done
awk -f $programdir/proganal $scratchdir/g09.log >> dynfollowfile
rm -f tempdone

```

```

tail -2 dynfollowfile | awk '/XXXX/ {print}' > tempdone
if (test -s tempdone) then
  if [ `awk '/reversetraj/ {if ($1=="reversetraj") print $2}' progdyn.conf` = "true" ];
then
  if [ `cat skipstart` = "reverse" ]; then
    rm -f skipstart
    rm -f geoPlusVel
    rm -f olddynrun
    rm -f olderdynrun
    a=`awk '{print $1}' isomernumber`
    mv traj traj$a
    mv dyn dyn$a
  fi
  if [ `cat skipstart` = "forward" ]; then
    echo reverserestart > skipstart
  fi
else
  rm -f skipstart
  rm -f geoPlusVel
  rm -f olddynrun
  rm -f olderdynrun
  a=`awk '{print $1}' isomernumber`
  mv traj traj$a
  mv dyn dyn$a
fi
if [ `cat skipstart` = "forward" ]; then
  echo reverserestart > skipstart
fi
else
  rm -f skipstart
  rm -f geoPlusVel
  rm -f olddynrun
  rm -f olderdynrun
  a=`awk '{print $1}' isomernumber`
  mv traj traj$a
  mv dyn dyn$a
fi
break
fi
done
#
END_of_C_Loop____END_of_C_Loop____END_of_C_Loop____END_of_C_Loop____
__END_of_C_Loop____END_of_C_Loop____

```

```

# We've got to break a second time to get out of this loop
# if we really want to quit. Otherwise, it will start over
# at the top
  if (test -f nogo) then
    break
  fi
  if (test -s goingwell) then
    echo "starting a new point or a new direction"
  else
    break
  fi
done
  if (test -f nogo) then
    break
  fi
  if (test -s goingwell) then
    echo "starting a new point or a new direction2"
  else
    break
  fi
done
exit 0

```

2. Program proggenHP

```

BEGIN {
# Aut 2010 changes classicalSpacing to 2 and upped possible excited states to 4000
# Jan 2009 - a number of little changes to improve reporting, precision, etc, specification
of displacement on particular modes
# Jan 2009 cannonball trajectories. adds desired energy to initial velocities based on file
cannontraj, so one can shoot toward a ts
# updated Nov 2008 to incorporate running DRPs
# updated Nov 2008 to allow for start without an initial freq calc using classical = 2
# updated Aug 2008 added to atom list to handle a large number of atoms without
changes needed
# updated June 2008 to incorporate new method for choosing displacements with
initialdis 2
# updated Jan 17 2008 - bug fix for > 99 atoms, 300 excitations of low modes possible
# version August 2007 - incorporates classical trajectory calculation option
#also allows listing of number of imaginary frequencies
# version Sept 16, 2005 - incorporates searchdir but not yet rotation
# now reads random numbers from temp811, starting at a random place
# The input files are generated before this and are tempfreqs, tempredmass,

```



```

# tempfr, tempmodes, and tempstangeos.
# It will count the number of atoms.

# default parameters, including quassiclassical, no displacements, transition state, not a
DRP
# do not change these - rather, change progdyn.conf to set the parameters
initialDis=0; timestep=1E-15; scaling=1.0; temp=298.15
classical=0; numimag=1; DRP=0; cannonball=0
charge=0; multiplicity=1; method="HF/3-21G"; memory=20000000
diag=1; checkpoint="g09.chk"; searchdir="positive"; boxon=0
boxsize=10; maxAtomMove=0.1; title1="you"; title2="need"
title3="a"; title4="progdyn.conf"; processors=1; highlevel=999
conver1=4.184E26 #dividing by this converts amu ang2 /s2 to kcal/mol

#initialization and constants
for (i=1;i<=10000;i++) {disMode[i]=-1}
i=1;j=1;k=1
c=29979245800; h=6.626075E-34; avNum=6.0221415E23
RgasK=0.00198588; RgasJ=8.31447
numAtoms=0; atomnumber=0; classicalSpacing=2
zpeGauss=0; zpeGaussK=0; zpePlusE=0; potentialE=0

# read progdyn.conf for configuration info
blankLineTester=10
while (blankLineTester>1) {
  getline < "progdyn.conf"
  if ($1=="method") method=$2
  if ($1=="charge") charge=$2
  if ($1=="multiplicity") multiplicity=$2
  if ($1=="memory") memory=$2
  if ($1=="processors") processors=$2
  if ($1=="checkpoint") checkpoint=$2
  if ($1=="diagnostics") diag=$2
  if ($1=="initialdis") initialDis=$2
  if ($1=="timestep") timestep=$2
  if ($1=="scaling") scaling=$2
  if ($1=="temperature") temp=$2
  if ($1=="searchdir") searchdir=$2
  if ($1=="classical") classical=$2
  if ($1=="numimag") numimag=$2
  if ($1=="highlevel") highlevel=$2
  if ($1=="boxon") boxon=$2
  if ($1=="boxsize") boxsize=$2
}

```

```

if ($1=="DRP") DRP=$2; if (DRP==1) classical=2 #this lets one start a DRP from a
point that is not a freq calc
if ($1=="maxAtomMove") maxAtomMove=$2
if ($1=="cannonball") cannonball=$2
if ($1=="displacements") disMode[$2]=$3
if ($1=="controlphase") controlPhase[$2]=$3
if ($1=="title") {
    title1=$2
    title2=$3
    title3=$4
    title4=$5
}
blankLineTester=length($0)
}

```

```

if (diag>=1) print "***** starting proggen *****" >>
"diagnostics"
if (diag>=1) print "method,charge,multiplicity,memory" >> "diagnostics"
if (diag>=1) print method,charge,multiplicity,memory >> "diagnostics"
if (diag>=1) print "processors,checkpoint,title,initialdis,timestep,scaling,temperature" >>
"diagnostics"
if (diag>=1) print
processors,checkpoint,title1,title2,title3,title4,initialDis,timestep,scaling,temp >>
"diagnostics"
if (diag>=1) print
"classical,numimag,highlevel,boxon,boxsize,DRP,maxAtomMove,cannonball" >>
"diagnostics"
if (diag>=1) print
classical,numimag,highlevel,boxon,boxsize,DRP,maxAtomMove,cannonball >>
"diagnostics"

```

```

# put geometries into array, also figure out number of atoms
# note that this picks out the last geometry in a file, assuming
# that if there is an optimization followed by a freq, nothing else follows
# kludgy - repeats last line twice - must be a better way
do {
    getline < "tempstangeos"
    if (oldline==$0) $0=""
    oldline=$0
    atom = $1
    if (atom>numAtoms) numAtoms=atom
    atNum[atom]=$2
    geoArr[atom,1]=$4; geoArr[atom,2]=$5; geoArr[atom,3]=$6
    velArr[atom,1]=0; velArr[atom,2]=0; velArr[atom,3]=0
}

```

```

}
while (length($0) > 0)

#output the number of atoms, used in many routines
print numAtoms

# put in atomic symbols and atomic weights - assigns a default mass but then reads it
from tempmasses when possible
for (i=1;i<=numAtoms;i++) {
  getline < "tempmasses"
  if (atNum[i]==1) {atSym[i]="H";atWeight[i]=1.00783}
  if (atNum[i]==2) {atSym[i]="He";atWeight[i]=4.0026}
  if (atNum[i]==3) {atSym[i]="Li";atWeight[i]=6.941}
  if (atNum[i]==4) {atSym[i]="Be";atWeight[i]=9.012}
  if (atNum[i]==5) {atSym[i]="B";atWeight[i]=10.811}
  if (atNum[i]==6) {atSym[i]="C";atWeight[i]=12.}
  if (atNum[i]==7) {atSym[i]="N";atWeight[i]=14.007}
  if (atNum[i]==8) {atSym[i]="O";atWeight[i]=15.9994}
  if (atNum[i]==9) {atSym[i]="F";atWeight[i]=18.9984}
  if (atNum[i]==10) {atSym[i]="Ne";atWeight[i]=20.1797}
  if (atNum[i]==11) {atSym[i]="Na";atWeight[i]=22.989}
  if (atNum[i]==12) {atSym[i]="Mg";atWeight[i]=24.305}
  if (atNum[i]==13) {atSym[i]="Al";atWeight[i]=26.98154}
  if (atNum[i]==14) {atSym[i]="Si";atWeight[i]=28.0855}
  if (atNum[i]==15) {atSym[i]="P";atWeight[i]=30.9738}
  if (atNum[i]==16) {atSym[i]="S";atWeight[i]=32.066}
  if (atNum[i]==17) {atSym[i]="Cl";atWeight[i]=35.4527}
  if (atNum[i]==18) {atSym[i]="Ar";atWeight[i]=39.948}
  if (atNum[i]==19) {atSym[i]="K";atWeight[i]=39.0983}
  if (atNum[i]==20) {atSym[i]="Ca";atWeight[i]=40.078}
  if (atNum[i]==21) {atSym[i]="Sc";atWeight[i]=44.96}
  if (atNum[i]==22) {atSym[i]="Ti";atWeight[i]=47.867}
  if (atNum[i]==23) {atSym[i]="V";atWeight[i]=50.94}
  if (atNum[i]==24) {atSym[i]="Cr";atWeight[i]=51.9961}
  if (atNum[i]==25) {atSym[i]="Mn";atWeight[i]=54.938}
  if (atNum[i]==26) {atSym[i]="Fe";atWeight[i]=55.845}
  if (atNum[i]==27) {atSym[i]="Co";atWeight[i]=58.933}
  if (atNum[i]==28) {atSym[i]="Ni";atWeight[i]=58.693}
  if (atNum[i]==29) {atSym[i]="Cu";atWeight[i]=63.546}
  if (atNum[i]==30) {atSym[i]="Zn";atWeight[i]=65.38}
  if (atNum[i]==31) {atSym[i]="Ga";atWeight[i]=69.723}
  if (atNum[i]==32) {atSym[i]="Ge";atWeight[i]=72.64}
  if (atNum[i]==33) {atSym[i]="As";atWeight[i]=74.9216}
  if (atNum[i]==34) {atSym[i]="Se";atWeight[i]=78.96}
}

```

```

    if (atNum[i]==35) {atSym[i]="Br";atWeight[i]=79.904}
    if (atNum[i]==46) {atSym[i]="Pd";atWeight[i]=106.42}
    if (atNum[i]==53) {atSym[i]="I";atWeight[i]=126.90447}
# gets actual weight from freqinHP when possible so a prior calc with readisotopes gets
you isotopic substitution
    if ((i<100) && ($9>0)) atWeight[i]=$9
    if ((i>99) && ($8>0)) atWeight[i]=$8

    if ((diag>1) && (i==1)) print
"atNum[i],atSym[i],atWeight[i],geoArr[i,1],geoArr[i,2],geoArr[i,3]" >> "diagnostics"
    if (diag>1) print atNum[i],atSym[i],atWeight[i],geoArr[i,1],geoArr[i,2],geoArr[i,3] >>
"diagnostics"
    }

# read in frequencies, scale them, read in Reduced masses, read in force
#constants, replace negative frequencies by 2 wavenumbers
numFreq=3*numAtoms-6
for (i=1;i<=numFreq;i++) {
    $0=""
    getline < "tempfreqs"
    freq[i]=$0*scaling
    if (freq[i]<0) freq[i]=2
    }
for (i=1;i<=numFreq;i++) {
    $0=""
    getline < "tempredmass"
    redMass[i]=$0
    if (redMass[i]=="") redMass[i]=1.
    }
for (i=1;i<=numFreq;i++) {
    $0=""
    getline < "tempfrfc"
    frc[i]=$0
    if (frc[i]=="") frc[i]=0.0001
    if (frc[i]==0) frc[i]=0.0001
    if ((diag>1) && (i==1)) print "freq[i],redMass[i],frc[i]" >> "diagnostics"
    if (diag>1) print freq[i],redMass[i],frc[i] >> "diagnostics"
    }

# read in the modes - note that trajectories always need a freq calc with freq=hpmodes
unless classical=2
if (classical!=2) {
    for (i=1;i<=numFreq;i+=5) {
        for (j=1;j<=(3*numAtoms);j++) {

```

```

        getline < "tempmodes"
        mode[i,$2,$1]=$4; mode[i+1,$2,$1]=$5; mode[i+2,$2,$1]=$6;
mode[i+3,$2,$1]=$7; mode[i+4,$2,$1]=$8
    }
}
}
if (diag>2) {for (i=1;i<=numFreq;i++) {print mode[i,1,1],mode[i,1,2],mode[i,1,3] >>
"modesread"}}}

# if doing a cannonball trajectory, read in the vector
if (cannonball>0) {
    for (i=1;i<=numAtoms;i++) {
        getline < "cannontraj"
        cannonArr[i,1]=$1; cannonArr[i,2]=$2; cannonArr[i,3]=$3
    }
}

# collect a series of random numbers from file temp811, generated from an outside
random number generator called by prodynstarterHP
# read from temp811, starting at a random place
srand(); tester=rand()*1000
for (i=1;i<=tester;i++) getline < "temp811"
for (i=1;i<=numFreq;i++) {
    getline < "temp811"; randArr[i]=$1
    getline < "temp811"; randArrB[i]=$1
    getline < "temp811"; randArrC[i]=$1
}
# for a QM distribution for a harmonic oscillator in its ground state, we want to generate
a set of random numbers
#between -1 and 1 weighted such that numbers toward the center are properly more
common
i=1
while (i<=numFreq) {
    if ((initialDis==2) || (disMode[i]==2)) {
        getline < "temp811"
        tempNum=2*( $1-.5)
        prob=exp(-(tempNum^2))
        getline < "temp811"
        if ($1<prob) {
            randArrD[i]=tempNum
            i++
        }
    }
}
if ((initialDis!=2) && (disMode[i]!=2)) i++

```

```

    }

# to start without normal modes or frequencies we need to just pick a random direction
for the motion of each atom, requiring 3N random numbers
for (i=1;i<=numAtoms;i++) {
  for (j=1;j<=3;j++) {
    getline < "temp811"
    if ($1>0.5) randArrE[i,j]=1
    if ($1<.5) randArrE[i,j]=-1
  }
}

# determine energy in each normal mode
for (i=1;i<=numFreq;i++) {
  zpeJ[i]=0.5*h*c*freq[i]    #units J per molecule
#if classical, treat as modes spaced by classicalSpacing wavenumbers
  if (classical==1) zpeJ[i]=0.5*h*c*classicalSpacing # the zpe is not used when
classical but the spacing is used to calculate the E in mode
  zpeK[i]=zpeJ[i]*avNum/4184 #units kcal/mol
  if (temp<10) vibN[i]=0    # avoids working with very small temperatures - if the
temp is too low, it just acts like 0 K
  if (temp>=10) {
    zpeRat[i]=exp((-2*zpeK[i])/(RgasK*temp))
    if (zpeRat[i]==1) zpeRat[i]=.99999999999
    Q[i]=1/(1-zpeRat[i])
    newRand=randArr[i]
    vibN[i]=0
    tester=1/Q[i]
#   get up to 4000 excitations of low modes
    for (j=1;j<=(4000*zpeRat[i]+2);j++) {
      if (newRand>tester) vibN[i]++
      tester=tester+((zpeRat[i]^j)/Q[i])
    }
  }
}

# figure out mode energies and maximum classical shift and then actual shift
# also calculated total energy desired for molecule
desiredModeEnK=0
for (i=1;i<=numFreq;i++) {
  modeEn[i]=(zpeJ[i]*1E18)*(2*vibN[i]+1) # units here are mDyne Angstroms for
compatibility with Gaussian force constants
  if (classical==1) modeEn[i]=(zpeJ[i]*1E18)*2*vibN[i] #no zpe when classical
  modeEnK[i]=zpeK[i]*(2*vibN[i]+1)
}

```

```

    if (classical==1) modeEnK[i]=zpeK[i]*2*vibN[i]      #no zpe when classical
    desiredModeEnK=desiredModeEnK + modeEnK[i]
# no 1/2 hv for imaginary frequencies
# treating modes with frequencies <10 as translations, ignoring their zero point energies
    if (freq[i]<10) modeEn[i]=(zpeJ[i]*1E18)*(2*vibN[i])
    maxShift[i]=(2*modeEn[i]/frc[i])^0.5
    if (initialDis==2) shift[i]=maxShift[i]*randArrD[i]
    if (initialDis==1) shift[i]=maxShift[i]*(2*(randArrC[i]-0.5))
    if (initialDis==0) shift[i]=0
# lines below allow for setting of displacement mode for individual modes
# It used to be necessary to use disMode 10 to turn off displacements for a mode, but
hopefully that bug is killed and you can use disMode 0
    if (disMode[i]==2) shift[i]=maxShift[i]*randArrD[i]
    if (disMode[i]==1) shift[i]=maxShift[i]*(2*(randArrC[i]-0.5))
    if (disMode[i]==10) shift[i]=0 #kept for backward compatability
    if (disMode[i]==0) shift[i]=0
# no displacements along imaginary frequencies and very low ones - it is better to treat
these
# as translations - employing a shift can give you initial weird geometries
    if (freq[i]<10) shift[i]=0
    if (numimag==1) shift[1]=0
    if (numimag==2) shift[2]=0
    }
for (i=1;i<=numFreq;i++) {
    if ((diag>1) && (i==1)) print
"zpeJ[i],zpeK[i],zpeRat[i],Q[i],vibN[i],modeEn[i],maxShift[i],shift[i]" >> "diagnostics"
    if (diag>1) print zpeJ[i],zpeK[i],zpeRat[i],Q[i],vibN[i],modeEn[i],maxShift[i],shift[i]
>> "diagnostics"
    }

# multiply each of the modes by its shift and add them up
# Do not do this if classical=2
if (classical!=2) {
    for (i=1;i<=numFreq;i++) {
        for (j=1;j<=numAtoms;j++) {
            for (k=1;k<=3;k++) {
                shiftMode[i,j,k]=mode[i,j,k]*shift[i]
                geoArr[j,k]=geoArr[j,k]+shiftMode[i,j,k]
            }
        }
    }
}

#now start toward velocities

```

```

for (i=1;i<=numFreq;i++) {
  kinEn[i]=100000*(modeEn[i]-0.5*frc[i]*shift[i]^2) # the 100000 converts to g
angstrom^2 s^2
  vel[i]=(2*kinEn[i]/(redMass[i]/avNum))^0.5 # in angstrom / s
#use searchdir in progdyn.conf to control the direction for trajectories started from a
saddle point
  if (numimag>1) numimag=1 #only the first freq can be sent in the searchdir direction,
the rest go in a random direction
  if (i>numimag) {
    if (randArrB[i]<0.5) vel[i]=-vel[i]
  }
  if (i==numimag) {
    if (searchdir=="negative") vel[i]=-vel[i]
  }
  if ((diag>1) && (i==1)) print "vel[i]" >> "diagnostics"
  if (diag>1) print vel[i] >> "diagnostics"
}

# if controlphase is being used, set the velocity on particular modes as positive or
negative as requested
for (i=1;i<=numFreq;i++) {
  if ((controlPhase[i]=="positive") && (vel[i]<0)) vel[i]=-vel[i]
  if ((controlPhase[i]=="negative") && (vel[i]>0)) vel[i]=-vel[i]
}

# multiply each of the modes by its velocity and add them up
# Do not do this if classical=2
if (classical!=2) {
  for (i=1;i<=numFreq;i++) {
    for (j=1;j<=numAtoms;j++) {
      for (k=1;k<=3;k++) {
        velMode[i,j,k]=mode[i,j,k]*vel[i]*timestep
        velArr[j,k]=velArr[j,k]+velMode[i,j,k]
      }
    }
  }
}

# to start without normal modes or frequencies we figure out the energy per atom based
on 1/2RT in degree of freedom
if (classical==2) {
  degFreedomEnK=temp*RgasK
  degFreedomEnJ=degFreedomEnK/(avNum/4184)
  cartEn=degFreedomEnJ*1E18
}

```



```

kinEnCart=100000*cartEn
#print degFreedomEnK, degFreedomEnJ, cartEn, kinEnCart
for (i=1;i<=numAtoms;i++) {
  for (j=1;j<=3;j++) {
    velArr[i,j]=randArrE[i,j]*timestep*(2*kinEnCart/(atWeight[i]/avNum))^0.5
    if (DRP==1) velArr[i,j]=0
  }
}

# calculate the KE in the modes at this point
KEinitmodes=0
for (j=1;j<=numAtoms;j++) {
  KEinitmodes=KEinitmodes + 0.5*atWeight[j]*(velArr[j,1]^2 + velArr[j,2]^2 +
velArr[j,3]^2)/((timestep^2)*conver1)
}

# if doing a cannonball, adjust multiplier until extra energy is correct
if (cannonball>0) {
  multiplier=1; tester=0; tolerance=.1
  while (tester==0) {
    KEinittotal=0
    for (j=1;j<=numAtoms;j++) {
      cannonvelArr[j,1]=velArr[j,1]+multiplier*cannonArr[j,1];
cannonvelArr[j,2]=velArr[j,2]+multiplier*cannonArr[j,2];
cannonvelArr[j,3]=velArr[j,3]+multiplier*cannonArr[j,3]
      KEinittotal=KEinittotal + 0.5*atWeight[j]*(cannonvelArr[j,1]^2 +
cannonvelArr[j,2]^2 + cannonvelArr[j,3]^2)/((timestep^2)*conver1)
    }
    if (KEinittotal>(KEinitmodes+cannonball+tolerance))
multiplier=multiplier*0.98901364
    if (KEinittotal<(KEinitmodes+cannonball-tolerance)) multiplier=multiplier*1.01
    if ((KEinittotal<(KEinitmodes+cannonball+tolerance)) &&
(KEinittotal>(KEinitmodes+cannonball-tolerance))) tester=1
  }
  for (j=1;j<=numAtoms;j++) {
    velArr[j,1]=velArr[j,1]+multiplier*cannonArr[j,1];
velArr[j,2]=velArr[j,2]+multiplier*cannonArr[j,2];
velArr[j,3]=velArr[j,3]+multiplier*cannonArr[j,3]
  }
}

#output the new geometry.

```

```

# ***** this section changed for special experiment for cyclopentadiene. do not use
this for other cases
# atWeight[4]=140.0001
# ***** line below added for special experiment switching mass from 12 to 140,
keeping momenta the same
#velArr[4,1]=velArr[4,1]/11.66667; velArr[4,2]=velArr[4,2]/11.66667;
velArr[4,3]=velArr[4,3]/11.66667
for (j=1;j<=numAtoms;j++) {
  printf("%2s % .7f % .7f % .7f %9.5f
\n",atSym[j],geoArr[j,1],geoArr[j,2],geoArr[j,3],atWeight[j])
}

#output the velocities and calculate the total kinetic energy overall
KEinittotal=0
for (j=1;j<=numAtoms;j++) {
  KEinittotal=KEinittotal + 0.5*atWeight[j]*(velArr[j,1]^2 + velArr[j,2]^2 +
velArr[j,3]^2)/((timestep^2)*conver1)
  printf("% .8f % .8f % .8f \n",velArr[j,1],velArr[j,2],velArr[j,3])
}

#anything else I add to the file will not affect the trajectories but will keep a record and
be good for analysis
for (i=1;i<=numFreq;i++) {
  if (initialDis==0) printf("% .6f % .6f %4i % 1.4e % .6f %1i\n", randArr[i],
randArrB[i], vibN[i], vel[i], shift[i], disMode[i])
  if (initialDis==1) printf("% .6f % .6f %4i % 1.4e % .6f %1i\n", randArr[i],
randArrC[i], vibN[i], vel[i], shift[i], disMode[i])
  if (initialDis==2) printf("% .6f % .6f %4i % 1.4e % .6f %1i\n", randArr[i],
randArrD[i], vibN[i], vel[i], shift[i], disMode[i])
}
print "temp ",temp
print "initialDis",initialDis
print "classical",classical
print "timestep",timestep
print "numimag",numimag
OFMT = "%.3f"
print "Total mode energy desired=",desiredModeEnK
print "KE initial from modes=",KEinitmodes," KE initial total=",KEinittotal
if (cannonball>0) print "cannonball",cannonball," cannon Energy=",KEinittotal-
KEinitmodes
if (boxon>0) print "boxsize",boxsize
if (DRP>0) print "DRP",DRP," maxAtomMove",maxAtomMove
if (DRP>0) print maxAtomMove > "maxMove"
} # End of BEGIN

```

```

/Zero-point correction/ {zpeGauss=$3}
/zero-point Energies/ {zpePlusE=$7}
END {
zpeGaussK=zpeGauss*627.509
potentialE=zpePlusE - zpeGauss
OFMT = "%.6f"
print "Gaussian zpe=",zpeGauss,"or",zpeGaussK,"kcal/mol E + zpe=",zpePlusE,"
potential E=",potentialE
print "" #will use blank line to mark end of geoPlusVel file
}

```

3. Program prog1stpoint

```

BEGIN {
# aug 2010 changed so that it is more careful in reading in from geoPlusVel
# removed some default parameters that should always be defined
# Jan 2009 - a number of little changes to improve reporting, precision, etc
# aug 2008 added to atom list so handles H to Cl without change needed
# version Feb 2008 incorporates methodfile, boxon and boxsize, though this point
unaffected by box
# version Jan 2008 - allows for ONIOM jobs, fixed atoms
# version Sept 2005 - incorporates meth3, meth4, meth5, meth6, but not yet rotation
# this program creates the first input file for g09
# the title should be changed as appropriate
# the isomer number comes from a file isomernumber

# default parameters, including quassiclassical, no displacements, transition state, not a
DRP
# do not change these - rather, change progdyn.conf to set the parameters
initialDis=0; timestep=1E-15; scaling=1.0; temp=298.15
classical=0; numimag=1; DRP=0; cannonball=0
memory=20000000
diag=1; checkpoint="g09.chk"; searchdir="positive"; boxon=0
boxsize=10; maxAtomMove=0.1; title1="you"; title2="need"
title3="a"; title4="progdyn.conf"; processors=1; highlevel=999

#initialization
i=1;j=1;k=1
c=29979245800; h=6.626075E-34; avNum=6.0221415E23
RgasK=0.00198588; RgasJ=8.31447
numAtoms=0; atomnumber=0

# read progdyn.conf for configuration info

```

```

blankLineTester=10
while (blankLineTester>1) {
  getline < "progdyn.conf"
  if ($1=="method") method=$2
  if ($1=="method2") meth2=$2
  if ($1=="charge") charge=$2
  if ($1=="multiplicity") multiplicity=$2
  if ($1=="memory") memory=$2
  if ($1=="processors") processors=$2
  if ($1=="checkpoint") checkpoint=$2
  if ($1=="timestep") timestep=$2
  if ($1=="diagnostics") diag=$2
  if ($1=="method3") meth3=$2
  if ($1=="method4") meth4=$2
  if ($1=="method5") meth5=$2
  if ($1=="method6") meth6=$2
  if ($1=="highlevel") highlevel=$2
  if ($1=="fixedatom1") fixedatom1=$2
  if ($1=="fixedatom2") fixedatom2=$2
  if ($1=="fixedatom3") fixedatom3=$2
  if ($1=="fixedatom4") fixedatom4=$2
  if ($1=="methodfile") methodfilelines=$2
  if ($1=="killcheck") killcheck=$2
  if ($1=="title") {
    title1=$2
    title2=$3
    title3=$4
    title4=$5
  }
  blankLineTester=length($0)
}

if (diag==1) print "***** starting prog1stpoint *****" >>
"diagnostics"
if (diag==1) print "method,charge,multiplicity,memory" >> "diagnostics"
if (diag==1) print method,charge,multiplicity,memory >> "diagnostics"
if (diag==1) print "processors,checkpoint,title" >> "diagnostics"
if (diag==1) print processors,checkpoint,title1,title2,title3,title4 >> "diagnostics"

getline < "isomernumber"
isomernum = $1
#read in number of atoms, geometry, masses, and velocity from geoPlusVel
getline < "geoPlusVel"
numAtoms=$1

```

```

# geometry
for (i=1;i<=numAtoms;i++) {
  getline < "geoPlusVel"
  weight[i]=$5
  atSym[i]=$1
  for (j=1;j<=3;j++) {
    geoArr[i,j]=$ (1+j)
  }
}
#velocities not needed for 1st point
for (i=1;i<=numAtoms;i++) {
  getline < "geoPlusVel"
  for (j=1;j<=3;j++) {
    velArr[i,j]=$j
  }
}

print "%nproc=" processors
print "%mem=" memory
if (killcheck!=1) print "%chk=" checkpoint
print "# " method " force scf=(tight,nosym) "
if (meth2=="unrestricted") print "guess=mix" #for unrestricted calculations
if (length(meth3)>2) print meth3
if (length(meth4)>2) print meth4
print ""
# make the title four words exactly, leaving out spaces if necessary
print title1,title2,title3,title4
print "runpoint 1"
print "runisomer ", isomernum
print ""
print charge,multiplicity
}

END {
for (i=1;i<=numAtoms;i++) {
  printf("%s %.7f %.7f %.7f",atSym[i],geoArr[i,1],geoArr[i,2],geoArr[i,3])
  if (i>highlevel) printf(" %s", "M")
  print ""
}
print ""
if (length(meth5)>2) print meth5
if (length(meth6)>2) print meth6
if (methodfilelines>=1) {
  for (i=1;i<=methodfilelines;i++) {

```

```

    getline < "methodfile"
    print $0
  }
}
print ""
}

```

4. Program prog2ndpoint

```

BEGIN {
#Aug 2010 added etolerance to make it controllable from progdyn.conf, made it so that
DRP does not check energy
# aug 2008 added to atom list so handles 1 to 17 without change needed
# version Feb 2008 incorporates methodfile, boxon and boxsize, though this point
unaffected by box
# version Jan 2008 - allows for ONIOM jobs, fixed atoms
# version Sept 9, 2005 - incorporates meth3, meth4, meth5, meth6, but not yet rotation
# read progdyn.conf for configuration info

# default parameters, including quassiclassical, no displacements, transition state, not a
DRP
# do not change these - rather, change progdyn.conf to set the parameters
initialDis=0; timestep=1E-15; scaling=1.0; temp=298.15
classical=0; numimag=1; DRP=0; cannonball=0
memory=20000000
diag=1; checkpoint="g09.chk"; searchdir="positive"; boxon=0
boxsize=10; maxAtomMove=0.1; title1="you"; title2="need"
title3="a"; title4="progdyn.conf"; processors=1; highlevel=999
etolerance=1

#initialization
i=1;j=1;k=1
c=29979245800; h=6.626075E-34; avNum=6.0221415E23
RgasK=0.00198588; RgasJ=8.31447
numAtoms=0; atomnumber=0

blankLineTester=10
while (blankLineTester>1) {
  getline < "progdyn.conf"
  if ($1=="method") method=$2
  if ($1=="method2") meth2=$2
  if ($1=="charge") charge=$2
  if ($1=="multiplicity") multiplicity=$2
  if ($1=="memory") memory=$2
  if ($1=="processors") processors=$2
}
}

```

```

if ($1=="checkpoint") checkpoint=$2
if ($1=="timestep") timestep=$2
if ($1=="diagnostics") diag=$2
if ($1=="method3") meth3=$2
if ($1=="method4") meth4=$2
if ($1=="method5") meth5=$2
if ($1=="method6") meth6=$2
if ($1=="highlevel") highlevel=$2
if ($1=="fixedatom1") fixedatom1=$2
if ($1=="fixedatom2") fixedatom2=$2
if ($1=="fixedatom3") fixedatom3=$2
if ($1=="fixedatom4") fixedatom4=$2
if ($1=="DRP") DRP=$2
if ($1=="methodfile") methodfilelines=$2
if ($1=="killcheck") killcheck=$2
if ($1=="etolerance") etolerance=$2
if ($1=="reversetraj") reversetraj=$2
if ($1=="title") {
    title1=$2
    title2=$3
    title3=$4
    title4=$5
}
blankLineTester=length($0)
}

```

```

if (diag>=1) print "***** starting prog2ndpoint *****" >>
"diagnostics"
if (diag>=1) print "method,charge,multiplicity,memory" >> "diagnostics"
if (diag>=1) print method,charge,multiplicity,memory >> "diagnostics"
if (diag>=1) print "processors,checkpoint,title" >> "diagnostics"
if (diag>=1) print processors,checkpoint,title1,title2,title3,title4 >> "diagnostics"

```

```

#get the isomer number from file
getline < "isomernumber"
isomernum = $1

```

```

#get forward or reverse from skipstart if it exists
getline < "skipstart"
trajdirection = $1

```

```

print "%nproc=" processors
print "%mem=" memory
if (killcheck!=1) print "%chk=" checkpoint

```

```

print "# " method " force scf=(tight,nosym) "
if (meth2=="unrestricted") print "guess=mix" #for unrestricted calculations
if (meth2=="read") print "guess=tcheck" #for reading orbitals from check, sometimes
faster, sometimes not
if (length(meth3)>2) print meth3
if (length(meth4)>2) print meth4
print ""
print title1,title2,title3,title4
print "runpoint 2"
print "runisomer ", isomernum
print ""
print charge,multiplicity

# ok, now we have to figure the second point. this should be
#  $x(t) = x + v*t + 1/2*F*t^2/m$ 
# so we need to set up arrays for position, velocity, and force

#read in number of atoms, geometry, masses, and velocity from geoPlusVel
getline < "geoPlusVel"
numAtoms=$1
# geometry
for (i=1;i<=numAtoms;i++) {
  getline < "geoPlusVel"
  weight[i]=$5
  atSym[i]=$1
  for (j=1;j<=3;j++) {
    geoArr[i,j]=$ (1+j)
  }
}
#velocities
for (i=1;i<=numAtoms;i++) {
  getline < "geoPlusVel"
  for (j=1;j<=3;j++) {
    velArr[i,j]=$j
  }
}

#now we go ahead and add the velocities
for (i=1;i<=numAtoms;i++) {
  for (j=1;j<=3;j++) {
    arr[i,j]=velArr[i,j]+geoArr[i,j]
    if (trajdirection=="reverserestart") arr[i,j]=geoArr[i,j]-velArr[i,j]
  }
  if ((diag>1) && (i==1)) print "geometry after adding velocities" >> "diagnostics"
}

```



```

    if (diag>1) print arr[i,1],arr[i,2],arr[i,3] >> "diagnostics"
  }

#pull out other information useful for testing whether total energy is right or bad
blankLineTester=10
while (blankLineTester>1) {
  getline < "geoPlusVel"
  if ($4=="desired=") desiredModeEnK=$5
  if ($4=="modes=") {
    KEinitmodes=$5
    KEinittotal=$9
  }
  if ($11=="potential") potentialE=$13
  blankLineTester=length($0)
}
#get initial geometry into file traj
print numAtoms >> "traj"
print potentialE,title1,title2,title3,title4,"runpoint 1 ", "runisomer ",isomernum >> "traj"
for (i=1;i<=numAtoms;i++) {
  print atSym[i],geoArr[i,1],geoArr[i,2],geoArr[i,3] >> "traj"
}
} # end of BEGIN

#pull out the potential energy
/SCF Done/ || /EUMP2 =/ || / Energy=/ {
if (($1=="Energy=") && ($3=="NIter=")) newPotentialE=$2
if ($1=="SCF") newPotentialE=$5
if ($1=="E2") {
  tempstring=$6
  split(tempstring, arr10, "D")
  newPotentialE=arr10[1]*(10^arr10[2])
}
newPotentialEK=(newPotentialE-potentialE)*627.509
}

# now we go ahead and translate the forces and add them
(/ 1 /||/ 2 /||/ 3 /||/ 4 /||/ 5 /||/ 6 /||/ 7 /||/
8 /||/ 9 /||/ 10 /||/ 11 /||/ 12 /||/ 13 /||/ 14 /||/
15 /||/ 16 /||/ 17 /||/ 18 /||/ 19 /||/ 20 /||/ 21 /||/
22 /||/ 23 /||/ 24 /||/ 25 /||/ 26 /||/ 27 /||/ 28 /||/
29 /||/ 30 /||/ 31 /||/ 32 /||/ 33 /||/ 34 /||/ 35 /) &&
length($3) > 9 {
i=$1
for (j=1;j<=3;j++) {

```

```

    forceArr[i,j]=$ (2+j) #the raw units of the forces are Hartree/Bohr
  }
  if ((diag>1) && (i==1)) print "i,weight[i],forceArr[i,1],forceArr[i,2],forceArr[i,3]" >>
  "diagnostics"
  if (diag>1) print i,weight[i],forceArr[i,1],forceArr[i,2],forceArr[i,3] >> "diagnostics"
}

END {
#put out Echeck but only if not a DRP
if (DRP==0) {
  print "trajectory #",isomernum >> "Echeck"
  print "point 1 potential E=",newPotentialEK," point 1 kinetic E=",KEinittotal,"
  Total=",newPotentialEK+KEinittotal >> "Echeck"
  print "desired total energy=", desiredModeEnK >> "Echeck"
  if ((newPotentialEK+KEinittotal)>(desiredModeEnK+etolerance)) print "XXXX bad
  total Energy" >> "Echeck"
  if ((newPotentialEK+KEinittotal)<(desiredModeEnK-etolerance)) print "XXXX bad
  total Energy" >> "Echeck"
}
# turn the forces into motion
for (i=1;i<=numAtoms;i++) {
  for (j=1;j<=3;j++) {
# conversions here take force to J/angstrom, 1E20 converts to kg angstroms / s^2, then
mult time (s^s) and divide by weight in kg to get angstroms

forceArr[i,j]=0.5*1E20*forceArr[i,j]*627.509*(4184/(0.529177*avNum))*(timestep^2)/
(weight[i]/(avNum*1000))
# for simplicity, DRPs will throw away the forces at the second pont. This means that if
we are not at a saddlepoint, point 2 = point 1 but this is a minor waste
  if (DRP==1) forceArr[i,j]=0
  arr[i,j]=arr[i,j]+forceArr[i,j]
# if atoms are fixed, replace calcd new position by original position
  if ((i==fixedatom1) || (i==fixedatom2) || (i==fixedatom3) || (i==fixedatom4))
arr[i,j]=geoArr[i,j]
  }
  if ((diag>1) && (i==1)) print "i,weight[i],forceArr[i,1],forceArr[i,2],forceArr[i,3]" >>
  "diagnostics"
  if (diag>1) print i,weight[i],forceArr[i,1],forceArr[i,2],forceArr[i,3] >> "diagnostics"
  printf("%s %.7f %.7f %.7f",atSym[i],arr[i,1],arr[i,2],arr[i,3])
  if (i>highlevel) printf(" %s", "M")
  print ""
  }
print ""
if (length(meth5)>2) print meth5

```

```

if (length(meth6)>2) print meth6
if (methodfilelines>=1) {
  for (i=1;i<=methodfilelines;i++) {
    getline < "methodfile"
    print $0
  }
}
print ""
#get second geometry into file traj
print numAtoms >> "traj"
print newPotentialE,title1,title2,title3,title4,"runpoint 2 ","runisomer ",isomernum >>
"traj"
for (i=1;i<=numAtoms;i++) {
  print atSym[i],arr[i,1],arr[i,2],arr[i,3] >> "traj"
}
}

```

5. Program progdynb

```

BEGIN { #this is the main routine for generating new .com files by the Verlet
algorithm
# Aug 2010 increased elements handled automatically but only up to bromine!
# Jan 2009 - a number of little changes to improve reporting, precision, etc
# Nov 2008 added ability to handle DRPs
# Aug 2008 added long list of atoms to handle 1-17 without change
# May 2008 added option to put out velocities in vellist - make diag=3
# version Feb 2008 incorporates methodfile, boxon and boxsize
# version Jan 2008 incorporates fixed atoms, oniom, and velocity damping
# version August 2007 incorporates keepevery to decrease size of dyn file
# version Sept 11, 2005 - incorporatates meth3, meth4, meth5, meth6, but not yet rotation

# default parameters, including quassiclassical, no displacements, transition state, not a
DRP
# do not change these - rather, change progdyn.conf to set the parameters
initialDis=0; timestep=1E-15; scaling=1.0; temp=298.15
classical=0; numimag=1; DRP=0; cannonball=0
memory=20000000
diag=1; checkpoint="g09.chk"; searchdir="positive"; boxon=0
boxsize=10; maxAtomMove=0.1; title1="you"; title2="need"
title3="a"; title4="progdyn.conf"; processors=1; highlevel=999
damping=1

#initialization
i=1;j=1;k=1

```

```

c=29979245800; h=6.626075E-34; avNum=6.0221415E23
RgasK=0.00198588; RgasJ=8.31447
numAtoms=0; atomnumber=0
conver1=4.184E26 #dividing by this converts amu ang2 /s2 to kcal/mol
OFS="  "

```

```

# read progdyn.conf for configuration info
blankLineTester=10
while (blankLineTester>1) {
  getline < "progdyn.conf"
  if ($1=="method") method=$2
  if ($1=="method2") meth2=$2
  if ($1=="charge") charge=$2
  if ($1=="multiplicity") multiplicity=$2
  if ($1=="memory") memory=$2
  if ($1=="processors") processors=$2
  if ($1=="checkpoint") checkpoint=$2
  if ($1=="timestep") timestep=$2
  if ($1=="diagnostics") diag=$2
  if ($1=="method3") meth3=$2
  if ($1=="method4") meth4=$2
  if ($1=="method5") meth5=$2
  if ($1=="method6") meth6=$2
  if ($1=="highlevel") highlevel=$2
  if ($1=="keepevery") keepevery=$2
  if ($1=="fixedatom1") fixedatom1=$2
  if ($1=="fixedatom2") fixedatom2=$2
  if ($1=="fixedatom3") fixedatom3=$2
  if ($1=="fixedatom4") fixedatom4=$2
  if ($1=="boxon") boxon=$2
  if ($1=="boxsize") boxsize=$2
  if ($1=="DRP") DRP=$2
  if ($1=="maxAtomMove") maxAtomMove=$2
  if ($1=="methodfile") methodfilelines=$2
  if ($1=="killcheck") killcheck=$2
  if ($1=="damping") damping=$2
  if ($1=="title") {
    title1=$2
    title2=$3
    title3=$4
    title4=$5
  }
  blankLineTester=length($0)
}

```

```

if (diag>=1) print "***** starting progdynb *****" >>
"diagnostics"
if (diag>=1) print "method,charge,multiplicity,memory" >> "diagnostics"
if (diag>=1) print method,charge,multiplicity,memory >> "diagnostics"
if (diag>=1) print "processors,checkpoint,title" >> "diagnostics"
if (diag>=1) print processors,checkpoint,title1,title2,title3,title4 >> "diagnostics"

# get number of atoms and weights from geoPlusVel, and previous geometries from old
and older
getline < "geoPlusVel"
numAtoms=$1
for (i=1;i<=numAtoms;i++) {
  getline < "geoPlusVel"
  weight[i]=$5; atSym[i]=$1
}

for (at=1;at<=numAtoms;at++) {
  getline < "old"
  oldarr[at,1]=$4; oldarr[at,2]=$5; oldarr[at,3]=$6
}

for (at=1;at<=numAtoms;at++) {
  getline < "older"
  olderarr[at,1]=$4; olderarr[at,2]=$5; olderarr[at,3]=$6
}

#for DRPs read in oldAdjForces and maxAtomMove
if (DRP==1) {
  for (at=1;at<=numAtoms;at++) {
    getline < "oldAdjForces"
    oldForce[at,1]=$1; oldForce[at,2]=$2; oldForce[at,3]=$3
  }
  getline < "maxMove"
  if (($1<maxAtomMove) && ($1>0)) maxAtomMove=$1
  if (maxAtomMove<0.000001) maxAtomMove=0.000001
}

# record atom velocities for IVR analysis. This is actually the velocity in the previous
run, which is the easiest to calculate.
getline < "isomernumber"
isomernum = $1
getline < "runpointnumber"
runpointnum = $1

```

```

if (diag==3) print "runpoint ",runpointnum-1,"runisomer ",isomernum >> "vellist"
for (at=1;at<=numAtoms;at++) {
  atomVel=((oldarr[at,1]-olderarr[at,1])^2 + (oldarr[at,2]-olderarr[at,2])^2
+(oldarr[at,3]-olderarr[at,3])^2)^.5
  KEatomstotal=KEatomstotal+0.5*weight[at]*(atomVel^2)/((timestep^2)*conver1)
  if (diag==3) print atomVel >> "vellist"
}
apparentTemp=KEatomstotal*2/(3*RgasK*numAtoms)
if (diag==4) print "KEatomstotal",KEatomstotal,"apparent Temperature",apparentTemp
>> "vellist"
}

#pull out the potential energy
/SCF Done/ || /EUMP2 =/ || / Energy=/ {
if (($1=="Energy=") && ($3=="NIter=")) newPotentialE=$2
if ($1=="SCF") newPotentialE=$5
if ($1=="E2") {
  tempstring=$6
  split(tempstring, arr10, "D")
  newPotentialE=arr10[1]*(10^arr10[2])
}
}

#must adjust next line for weird atoms
(/ 1 /||/ 2 /||/ 3 /||/ 4 /||/ 5 /||/ 6 /||/ 7 /||/
8 /||/ 9 /||/ 10 /||/ 11 /||/ 12 /||/ 13 /||/ 14 /||/
15 /||/ 16 /||/ 17 /||/ 18 /||/ 19 /||/ 20 /||/ 21 /||/
22 /||/ 23 /||/ 24 /||/ 25 /||/ 26 /||/ 27 /||/ 28 /||/
29 /||/ 30 /||/ 31 /||/ 32 /||/ 33 /||/ 34 /||/ 35 /) &&
length($3) > 9 {
i=$1
for (j=1;j<=3;j++) {
  forceArr[i,j]=$2+j) #the raw units of the forces are Hartree/Bohr
}
if ((diag>1) && (i==1)) print "i,weight[i],forceArr[i,1],forceArr[i,2],forceArr[i,3]" >>
"diagnostics"
if (diag>1) print i,weight[i],forceArr[i,1],forceArr[i,2],forceArr[i,3] >> "diagnostics"
}

END {
#####routine for DRPs#####
if (DRP==1) {
  maxForce=0;oscillTest=0
  for (i=1;i<=numAtoms;i++) {

```

```

    for (j=1;j<=3;j++) {
# conversions here take force to J/angstrom, 1E20 converts to kg angstroms / s^2, then
mult time (s^s) and divide by weight in kg to get angstroms

forceArr[i,j]=1E20*forceArr[i,j]*627.509*(4184/(0.529177*avNum))*(timestep^2)/(wei
ght[i]/(avNum*1000))
    oscillTest=oscillTest+forceArr[i,j]*oldForce[i,j]
    if (forceArr[i,j]>maxForce) maxForce=forceArr[i,j]
    if ((0-forceArr[i,j])>maxForce) maxForce=-forceArr[i,j]
    }
    if (i==1) printf("% .8f % .8f % .8f \n",forceArr[1,1],forceArr[1,2],forceArr[1,3]) >
"oldAdjForces"
    if (i>1) printf("% .8f % .8f % .8f \n",forceArr[i,1],forceArr[i,2],forceArr[i,3]) >>
"oldAdjForces"
    }
    print "oscillTest ",oscillTest >> "oldAdjForces"
    if (oscillTest<0) {
        maxAtomMove = maxAtomMove*0.5
        print maxAtomMove > "maxMove"
    }
    if (oscillTest>0) {
        maxAtomMove = maxAtomMove*1.2
        print maxAtomMove > "maxMove"
    }
    print "maxAtomMove ",maxAtomMove >> "oldAdjForces"
    forceMult=maxAtomMove/maxForce
    for (i=1;i<=numAtoms;i++) {
        for (j=1;j<=3;j++) {
            newarr[i,j]=oldarr[i,j]+forceMult*forceArr[i,j]
        }
    }
}
#####

#####normal routine for Verlet #####
if (DRP==0) {
    for (i=1;i<=numAtoms;i++) {
        for (j=1;j<=3;j++) {
# conversions here take force to J/angstrom, 1E20 converts to kg angstroms / s^2, then
mult time (s^s) and divide by weight in kg to get angstroms

forceArr[i,j]=1E20*forceArr[i,j]*627.509*(4184/(0.529177*avNum))*(timestep^2)/(wei
ght[i]/(avNum*1000))

```

```

    if ((diag>1) && (i==1)) print "i,weight[i],forceArr[i,1],forceArr[i,2],forceArr[i,3]"
  >> "diagnostics"
    if (diag>1) print i,weight[i],forceArr[i,1],forceArr[i,2],forceArr[i,3] >>
  "diagnostics"
    newarr[i,j]=oldarr[i,j]+damping*(oldarr[i,j]-olderarr[i,j])+forceArr[i,j]
    if ((i==fixedatom1) || (i==fixedatom2) || (i==fixedatom3) || (i==fixedatom4))
newarr[i,j]=oldarr[i,j]
#turn around atoms outside the box
    if (boxon==1) {
      if (newarr[i,j]>boxsize) if (oldarr[i,j]>olderarr[i,j])
newarr[i,j]=oldarr[i,j]+damping*(olderarr[i,j]-oldarr[i,j])+forceArr[i,j]
      if (newarr[i,j]<-1*boxsize) if (oldarr[i,j]<olderarr[i,j])
newarr[i,j]=oldarr[i,j]+damping*(olderarr[i,j]-oldarr[i,j])+forceArr[i,j]
    }
  }
}
}
#####

if ((runpointnum % keepevery)==0) system("cat g09.log >> dyn")
print "%nproc=" processors
print "%mem=" memory
if (killcheck!=1) print "%chk=" checkpoint
print "# " method " force scf=(maxcycle=200) "
if (meth2=="unrestricted") print "guess=mix" #for unrestricted calculations
if (meth2=="read") print "guess=tcheck" #for reading orbitals from check, sometimes
faster, sometimes not
print "pop=none "
if (length(meth3)>2) print meth3
if (length(meth4)>2) print meth4
print ""
print title1,title2,title3,title4
print "runpoint ",runpointnum
print "runisomer ",isomernum
if (DRP==1) print "maxForce and forceMult and
maxAtomMove",maxForce,forceMult,maxAtomMove
print ""
print charge,multiplicity
print numAtoms >> "traj"
print newPotentialE,title1,title2,title3,title4,"runpoint ",runpointnum,"runisomer
",isomernum >> "traj"
for (i=1;i<=numAtoms;i++) {
  printf("%s %.7f %.7f %.7f",atSym[i],newarr[i,1],newarr[i,2],newarr[i,3])
  printf("%s %.7f %.7f %.7f",atSym[i],newarr[i,1],newarr[i,2],newarr[i,3]) >> "traj"
}

```



```

print "" >> "traj"
if (i>highlevel) printf(" %s", "M")
print ""
}
print ""
if (length(meth5)>2) print meth5
if (length(meth6)>2) print meth6
if (methodfilelines>=1) {
  for (i=1;i<=methodfilelines;i++) {
    getline < "methodfile"
    print $0
  }
}
print ""
}

```

6. Program randgen

```

# c program
# this can be replaced by a more reliable random number
# generator when available on a system
#include <stdio.h>
#include <stdlib.h>

int a,b,c;
double d;

int product(int x, int y);

int main(void)
{
  int count=1;
  srand48(time (0));
  while (count<=10000)
  {
    d = drand48();
    printf ("%f\n", d);
    count++;
  }
  return 0;
}

```

7. Program proganal

```

BEGIN {
getline < "isomernumber"
isomer=$1
}
/ Dichlorovinylketone/ {
printf("%s %s %s %s %s %s  ",$1,$2,$3,$4,$6,$8)
runpoint=$6
}
/Standard orientation/,/Rotational constants/ {
if (($1>.5) && ($1<27)) {
A[$1]=$4;B[$1]=$5;C[$1]=$6
}
}
}

END {
C10C111=Distance(10,11)
C19C10=Distance(9,10)
S7C10=Distance(7,10)
printf("%s %.3f %s %.3f %s %.3f
", "C10C111",C10C111,"C19C10",C19C10,"S7C10",S7C10)
if (runpoint>500) {
print "Too many points. XXXXMT"
movedyn(isomer)
movetraj(isomer)
}
if (C19C10>2.1) {
print "Inversion Product XXXX"
movedyn(isomer)
movetraj(isomer)
}
if (C10C111>2.1) {
print "Retention Product XXXX"
movedyn(isomer)
movetraj(isomer)
}
if (S7C10>3.5) {
print "Floated off XXXX"
movedyn(isomer)
}
}

system("date '+%b:%d:%Y %T'")
system("tail -1 Echeck | grep XXXX")
}

```

```

function Distance(Atom1,Atom2) {
  return sqrt((A[Atom1]-A[Atom2])^2 + (B[Atom1]-B[Atom2])^2 + (C[Atom1]-
C[Atom2])^2)
}

function Angle(Atom1,Atom2,Atom3) {
  value=((-
Distance(Atom1,Atom3)^2+Distance(Atom1,Atom2)^2+Distance(Atom2,Atom3)^2)/(2
*Distance(Atom1,Atom2)*Distance(Atom2,Atom3)))
  return acos(value)
}

function asin(x) { return (180/3.141592)*atan2(x, sqrt(1-x*x)) }

function acos(x) { return (180/3.141592)*atan2(sqrt(1-x*x), x) }

function atan(x) { return (180/3.141592)*atan2(x,1) }

function Dihedral(Atom1,Atom2,Atom3,Atom4) {
  B1x=A[Atom2]-A[Atom1]
  B1y=B[Atom2]-B[Atom1]
  B1z=C[Atom2]-C[Atom1]
  B2x=A[Atom3]-A[Atom2]
  B2y=B[Atom3]-B[Atom2]
  B2z=C[Atom3]-C[Atom2]
  B3x=A[Atom4]-A[Atom3]
  B3y=B[Atom4]-B[Atom3]
  B3z=C[Atom4]-C[Atom3]
  modB2=sqrt((B2x^2)+(B2y^2)+(B2z^2))
# yAx is x-coord. etc of modulus of B2 times B1
  yAx=modB2*(B1x)
  yAy=modB2*(B1y)
  yAz=modB2*(B1z)
# CP2 is the crossproduct of B2 and B3
  CP2x=(B2y*B3z)-(B2z*B3y)
  CP2y=(B2z*B3x)-(B2x*B3z)
  CP2z=(B2x*B3y)-(B2y*B3x)
  termY=((yAx*CP2x)+(yAy*CP2y)+(yAz*CP2z))
# CP is the crossproduct of B1 and B2
  CPx=(B1y*B2z)-(B1z*B2y)
  CPy=(B1z*B2x)-(B1x*B2z)
  CPz=(B1x*B2y)-(B1y*B2x)
  termX=((CPx*CP2x)+(CPy*CP2y)+(CPz*CP2z))
  dihed4=(180/3.141592)*atan2(termY,termX)
}

```

```

return dihed4
}

function killdyn(isomer) {
    system("rm -f dyn")
}

```

8. progdyn.conf

```

#This is the configuration file for PROGDYN. This file is read by progdynstarterHP and
# the awk programs proggenHP, prog1stpoint, prog2ndpoint, and progdynb.
#The programs won't read anything past the first blank line,
#and this file must end with a blank line.
#The program has a number of default values but they are unlikely to be what you want.
#Do not delete lines - rather, comment out lines for unwanted options.
#The values here are read repeatedly and most can be changed in the middle of running
jobs
****The keywords are case sensitive. The following keywords should always be
defined:****
****method, charge, multiplicity, memory, processors, title
**** method --The following word is copied exactly to the gaussian input file.
method B3LYP/6-31+G**
**** method2 --The options here are restricted, unrestricted, and read. restricted is the
default
#If the method is U..., put unrestricted here and the .com files will have in them
guess=mix.
#If you put read here, the .com files will contain guess=tcheck, which sometimes makes
things faster, sometimes not.
#The use of read requires a specifically defined checkpoint file name using the keyword
checkpoint.
method2 restricted
charge -1
multiplicity 1
processors 4
**** memory --The following "word" is copied exactly to the gaussian input file after
%mem=.
memory 7200mb
**** killcheck and checkpoint -- You can use a specifically defined checkpoint file
name by putting
#the name after the keyword checkpoint. This is necessary if you use the read option
with method2.
#Defined checkpoint names are an unnecessary modest hassle and if you do not want to
bother, use killcheck 1

```

```
killcheck 1
#checkpoint dyn20.chk
**** diagnostics -- 0 prints out nothing extra, 1 (default) prints out extra stuff to a
#file "diagnostics", 2 adds more stuff, 3 adds velocities to a file "vellist"
#4 adds the apparent temperature to vellist, but this is meaningless with quasiclassical
calculations
diagnostics 0
**** title -- the title keyword must be followed by exactly four words
title Dichlorovinylketone quasiclassical trajectories 298.15
**** initialdis -- 0 (default) turns off displacement of the normal modes, so that all
trajectories start from the same place
# and only the energies and signs of the motion in the modes are randomized
# 1 gives a flat distribution of displacements where all of the possible values are equally
likely
# 2 (recommended) gives a QM-like gaussian distribution of displacements, so that
displacements in the middle are more likely than
# those at the end by 1/e
initialdis 0
**** timestep -- this is the time between points in the trajectory. Typical values would
be 1E-15 or 0.5E-15 or 0.25E-15
timestep 1E-15
**** scaling -- this lets you scale the gaussian frequencies by a constant
scaling 1.0
temperature 298.15
**** method3, method4, method5, and method6 -- These keywords let you add extra
lines to the gaussian input file.
#method3 and method4 add lines at the top of the input after the lines defining the
method, and
#this is useful to implement things like the iop for mPW1k
#method5 and method6 add lines after the geometry, after a blank line of course
#only a single term with no spaces can be added, one per method line. Here are some
examples to uncomment if needed
#method3 IOp(3/76=0572004280)
#method3 scrf=(pcm,solvent=ethanol)
#add the line below with big structures to get it to put out the distance matrix and the
input orientation
#method3 iop(2/9=2000)
method4 scrf=(pcm,solvent=ethanol)
#method5 radii=bondi
#method6
**** methodfile -- This keyword lets you add more complicated endings to gaussian
input files
#such as a gen basis set. Put after the keyword the number of lines in a file you create
called
```

```

#methodfile that contains the test you want to add to the end of the gaussian input
methodfile 0
**** numimag --This tells the program the number of imaginary frequencies in the
starting structure.
#if 0, treats as ground state and direction of all modes is random
#if 1, motion along the reaction coordinate will start out in the direction defined by
searchdir
#if 2, only lowest freq will go direction of searchdir and other imag mode will go in
random direction
numimag 0
**** searchdir -- This keyword says what direction to follow the mode associated with
the imaginary frequency.
#The choices are "negative" and "positive". Positive moves in the direction defined in
the gaussian frequency calculation
#for the imaginary frequency, while negative moves in the opposite direction. The
correct choice can be made either
#by a careful inspection of the normal modes and standard orientation geometry, or by
trial and error.
searchdir positive
**** classical -- for quassiclassical dynamics, the default, use 0. for classical dynamics,
use 1
#if there are no normal modes and the velocities are to be generated from scratch, use
classical 2
classical 0
**** DRP, saddlepoint, and maxAtomMove --to run a DRP use 'DRP 1' in the line
below, otherwise leave it at 0 or comment it out
#the treatment of starting saddlepoints is not yet implemented so use saddlepoint no
#if DRP shows oscillations then decrease maxAtomMove
DRP 0
saddlepoint no
maxAtomMove 0.01
**** cannonball -- The program can "fire" a trajectory from a starting position toward a
particular target, such as toward
#a ts. To use this, make a file cannontraj with numAtom lines and three numbers per
line that defines the vector
#for firing the trajectory, relative to the starting geometry's standard orientation. The
number following cannonball sets
#the extra energy being put into the structure in kcal/mol
#cannonball 10
**** keepevery --This tells the program how often to write the gaussian output file to
file dyn, after the first two points.
#Use 1 for most dynamics to start with, but use a higher number to save on disk space or
molden loading time.
keepevery 1

```

```
*** highlevel --For ONIOM jobs, the following line states the number of highlevel
atoms,
#which must come before the medium level atoms. Use some high value such as 999 if
not using ONIOM
highlevel 999
*** fixedatom1, fixedatom2, fixedatom3, and fixedatom4 - These fix atoms in space.
#Fixing one atom serves no useful purpose and messes things up, while fixing two atoms
#fixes one distance and fixing three has the effect of fixing three distances, not just two
#in current form fixed atoms only are meant to work with no displacements, that is,
initialdis=0
#fixedatom1 2
#fixedatom2 3
#fixedatom3 19
*** boxon and boxsize - With boxon 1, a cubic box is set such that atoms that reach the
edge
#are reflected back toward the middle. Useful for dynamics with solvent molecules.
This is a crude
#implementation that is ok for a few thousand femtoseconds but will not conserve
energy long term.
#Set the box size so as to fit the entire initial molecule but not have too much extra
room.
#The dimensions of the box are two times the boxsize, e.g. boxsize 7.5 leads to a box
that is 15 x 15 x 15 angstroms
#boxon 0
#boxsize 7.5
*** displacements -- This keyword lets you set the initialdis of particular modes by
using a series of lines of the format
# displacements NumberOfMode InitialDisForThatMode, as in the example below. You
should be able to do as many of these as you like
# you might consider this for rotations where a straight-line displacement goes wrong at
large displacements
# The choices for InitialDisForThatMode are 0, 1, 2, and 10, where 10 does the same
thing as 0 but is maintained for now because
# a previous version of the program had a bug that made 0 not work.
#displacements 1 10
*** etolerance --This sets the allowable difference between the desired energy in a
trajectory and the actual
#energy, known after point 1 from the potential energy + the kinetic energy in the initial
velocities.
#The unit is kcal/mol and 1 is a normal value for mid-sized organic systems. For very
large and floppy molecules, a larger value
#may be needed, but the value must stay way below the average thermal energy in the
molecule (not counting zpe).
#If initialdis is not 0 and few trajectories are being rejected, decrease the value.
```

etolerance 1

**** controlphase --It is sometimes useful to set the phase of particular modes in the initialization of trajectories.

#The format is controlphase numberOfModeToControl positive or controlphase numberOfModeToControl negative.

**** damping -- The damping keyword lets you add or subtract energy from the system at each point, by multiplying the velocities

#by the damping factor. A damping of 1 has no effect, and since you mostly want to change the energy slowly, normal values range

#from 0.95 to 1.05. The use of damping lets one do simulated annealing - you add energy until the structure is moving enough

#to sample the kinds of possibilities you are interested in, then you take away the energy slowly.

damping 1

**** reversetraj --This keyword sets the trajectories so that both directions from a transition state are explored.

#reversetraj true

#updated Aug 9, 2007 to include the possibility of classical dynamics by the keyword classical

#updated Jan 2008 to include fixed atoms, ONIOM jobs, keepevery, and box size

#update Feb 2008 to include methodfile parameter

updated Nov 2008 to allow for start without an initial freq calc using classical = 2

update Aug 2010 to include etolerance, damping controlphase and reversetraj

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VITA

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