# Ab Initio Calculations on the Formation and Rearrangement of Spiropentane

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The formation of spiropentane, by addition of singlet ($^1A_1$) methylene to methylenecyclopropane, and the unimolecular reactions of spiropentane have all been studied computationally. Benchmark calculations on two key biradicals were conducted by the multireference Mukherjee's coupled-cluster (MkCC) method. Various single-reference coupled-cluster methods and multireference second-order perturbation theory were then compared for accuracy against experimental data and the MkCC results. The object of the exercise was to get the best possible description of the potential energy surface for formation and reactions of spiropentane, as a prelude to molecular dynamics simulation of the reactions. The principal conclusions of the study were that none of the unimolecular reactions of spiropentane can be classified as pericyclic processes and that the observed stereoselectivities are probably of dynamical origin. A possible resolution of a disagreement between two studies on the dynamics of cyclopropanation reactions is also offered. Of the various approximate computational models evaluated in this study, the best fit came from a composite coupled-cluster approach in which the lower-energy result was selected from a restricted coupled-cluster and a broken-symmetry, unrestricted coupled-cluster calculation on each stationary point. However, such an approach is not strictly defensible, since coupled-cluster methods are not variational, and so further evaluation of its validity would be desirable.

## Introduction

The calculations described in this paper were conducted with two broad issues in mind. The first concerned the topic of nonstatistical dynamics. The system chosen for this study promises the opportunity to gain new insights into reaction dynamics, as described below. The studies reported here were intended to reveal the main features of the potential energy surface and to act as a guide to subsequent experiments and molecular dynamics (MD) simulations. The second principal goal of the study was to compare different strategies for carrying out moderately to highly correlated electronic-structure calculations on systems with substantial multireference character.

The formation of cyclopropanes by addition of singlet methylene to alkenes has a long and distinguished history in the development and testing of models for chemical kinetics.[1,2] The principal appeal of reactions in this class is that they are extremely exothermic (typically releasing ~100 kcal/mol kinetic energy) and so afford cyclopropanes that are inevitably vibrationally excited to energies far above the thresholds for further reaction. Among the important issues probed by these studies have been mechanisms of collisional deactivation of vibrationally excited molecules and, of particular relevance to the present work, whether the reactions of the chemically activated cyclopropanes are adequately described by statistical kinetic models such as the Rice Ramsperger Kassel Marcus (RRKM) theory.[1−5]

On this last topic, the conclusions from two apparently similar studies have been strikingly different. In 1968 Doering and co-workers added singlet $CD_2$ to methylenecyclopropane and checked the label distribution in the methylenecyclobutane product (see Scheme 1) for signs of reaction prior to complete intramolecular vibrational energy redistribution (IVR).[3] They concluded that the results were fully consistent with a statistical dynamical model, i.e., that IVR was complete prior to secondary reaction of the chemically activated spiropentane. By contrast, when Rynbrandt and Rabinovitch studied the cyclopropanation of a fluorinated vinylcyclopropane and looked for nonstatisticality in the subsequent $CF_2$ extrusion, they found evidence that the fragmentation *could* occur prior to complete IVR, especially for reactions run at high pressure.[4,5] The seeming discrepancy in these conclusions is all the more striking because the nonstatistical behavior seems to have occurred in the larger molecule—an outcome at odds with conventional understanding of reaction dynamics.[6]

In an early experimental study on reaction of singlet methylene with methylenecyclopropane, Frey and co-workers reported that the products of addition to the double bond depended on the pressure of the bath gas. At low pressure, allene (and, implicitly, ethylene) dominated.[7] At high pressure, the principal product was spiropentane.[8] A third product, methylenecyclobutane, was found to reach a maximum yield at a pressure of ~300 Torr. To fit the pressure dependence of the product yields, Frey et al. had to include two pathways to allene (+ ethylene): one came directly from the chemically activated spiropentane and the other from methylenecyclobutane.[7] From their data, these researchers could not determine whether the two routes to allene represented entirely distinct mechanisms or whether they shared a common intermediate. That is one of the questions addressed in the present work.

The outcomes of the Doering and Frey experiments, when conducted at the same pressure, are compared in Scheme 1. The methyl-substituted methylenecyclopropanes arise from

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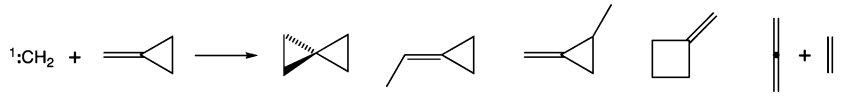
**SCHEME 1: Comparison of Product Ratios from the Experiments Reported by Doering et al.[3] and Frey et al.[7a]**




| | | | | | |
|---|---|---|---|---|---|
| Doering et al.: | 24% | 17% | 41% | 18% | None reported |
| Frey et al.: | 22% | 15% | 20% | 10% | 33% |

[a] The former ratios were reported to be pressure independent, whereas the latter were found to be pressure dependent. The values from the experiments of Frey et al. correspond to a pressure of 225 Torr.

C−H insertion of the methylene and are not of direct interest for the present work. Obviously, calculations cannot resolve the apparent discrepancy in purely experimental data. Nevertheless, as described at the end of this paper, the comparison of the two experiments does turn out to be useful for interpretation of the dynamical questions raised above.

## Computational Models and Methodology

For small organic systems such as those considered here, coupled-cluster calculations with moderately large basis sets are feasible and usually expected to give good results for the thermochemistry. However, there is one exception to this general rule: intermediates for which nondynamic electron correlation is very important, such a singlet biradicals, are known to be poorly described by single-reference methods such as conventional coupled-cluster theory.[9,10] As will be seen, the rearrangements and fragmentation of spiropentane are reactions that involve several different singlet biradicals, and so it was recognized from the outset that alternatives to simple coupled-cluster methods would need to be considered. In fact, this sequence of reactions looked as if it could provide an excellent test case for comparing different computational models because a good deal is known experimentally about the thermochemistry of these reactions.[11]

In all of the calculations described below (with the exception of the W1 calculations), geometry optimizations and vibrational frequencies were calculated with the cc-pVDZ basis set, and then higher-level single-point energy calculations were obtained with the cc-pVTZ basis set.[12]

An obvious choice of computational methods for reactions involving singlet biradicals would be one of the multireference second-order perturbation theory models. We have chosen the CASPT2 method of the Lund group, with the so-called g3 modification of the zeroth-order Hamiltonian.[13] These calculations were conducted with the MOLCAS program package.[14] To provide a consistent active space for the CASSCF reference wave function across all of the reactions considered here, the bonding and antibonding orbitals of all carbon−carbon bonds ($\pi$ and $\sigma$) were included, leading to a CASSCF(12,12) calculation. Geometries were optimized and vibrational frequencies calculated at this level.

Although single-reference coupled-cluster theory was expected to perform poorly for the singlet biradicals (and perhaps nearby transition structures), it was included as a comparison. Hence, RCCSD(T) calculations were carried out with an RHF reference wave function. Most of these calculations were carried out with the MOLPRO program package.[15] For these calculations, the geometries and vibrational frequencies were computed at the broken-symmetry UCCSD level described below.

In recent years, promising approaches for applying coupled-cluster theory to multireference systems have been reported. In general, these methods belong to the completely renormalized coupled-cluster class, of which there are several versions. We have used the so-called CR-CC(2,3) method.[16] These calculations were conducted with the GAMESS program.[17] Again, the broken-symmetry UCCSD geometries and frequencies were used.

A pragmatic and widely used (although sometimes controversial) method for handling singlet biradicals is the use of broken-symmetry unrestricted density functional theory (DFT).[18] What makes the method controversial is the apparent severe spin contamination that results. Calculated $\langle S^2 \rangle$ values for singlet biradicals are usually closer to 1 than to the correct value of 0. On the other hand, remarkably good agreement with experiment is frequently reported, with[19] or without[20] correction of the results for the apparent spin contamination. There is no particular reason to think that this general approach should be limited to DFT methods. In fact it has been used with coupled-cluster theory in a study on singlet *para*-benzyne and has led to encouraging results.[21] Cremer has argued that when high-level methods for handling dynamic correlation, such as CCSD or CCSD(T), are used, spin contamination from the broken-symmetry UHF reference wave function is almost completely eliminated, although a metric other than $\langle S^2 \rangle$ has to be computed to see the effect.[22] In the present work, geometries and vibrational frequencies were computed at the broken-symmetry (BS) UCCSD level, and then single-point calculations were carried out at the BS-UCCSD(T) level with the larger basis set. These calculations were conducted with the Gaussian03 program package.[23]

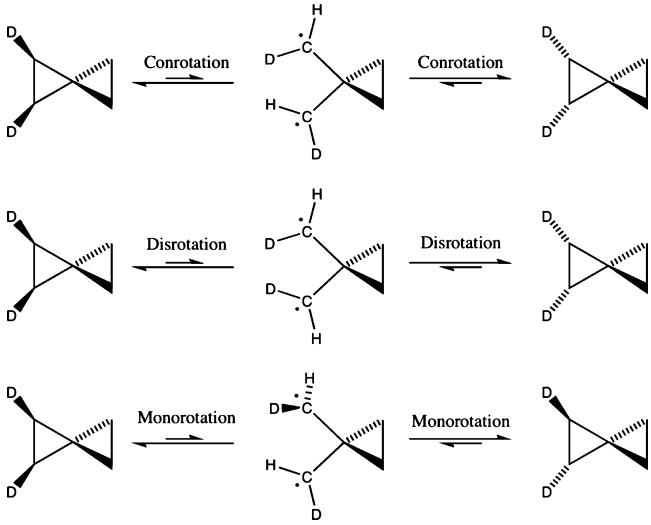
Perhaps the most promising approach of all to problems of the kind offered by the present set of reactions is to use a multireference coupled-cluster model. Several such calculations are being explored.[9,10,24−36] In the present case, we have employed the multireference Mukherjee's CC method[24,27,30] recently implemented at the SD(T) level (MkCCSD(T)),[28] using geometries optimized at the CASSCF(12,12)/cc-pVDZ level. The MkCC method is exactly size-extensive, in contrast to the a posteriori corrected Brillouin−Wigner MRCC method employed in previous studies.[25,29,35] It was thus a preferable choice in this work, where the MRCC result serves as a benchmark for comparison of several single-reference based computational approaches.

Since the MkCC method yields energies very similar to the single-reference counterpart if one reference configuration dominates, we avoided the unnecessary computational cost to apply them to all stationary points on the PE surface. Instead, we have used this approach to get the best estimates for the heats of formation of the possible biradical intermediates in the reactions of interest.

## Results and Discussion

**Formation of Spiropentane from Methylene and Methylenecyclopropane.** None of the computational models explored in the present work led to the prediction of a barrier for addition of singlet methylene to methylenecyclopropane. The failure to

**SCHEME 2: Possible Stereomutation Pathways for Spiropentane-*cis*-1,2-$d_2$[a]**




[a] The disrotation and monorotation reactions will also generate biradicals in which H and D locations are interchanged on both acyclic methylenes.

find a transition structure for this reaction would be in keeping with other calculations that have been carried out on methylene addition to alkenes and alkynes, which also find no barriers.[37,38]

The most recent experimental heat of formation for the *a* state ($^1A_1$) of methylene[39] is 102.5 ± 0.5 kcal/mol at 298 K, while those for methylenecyclopropane[40] and spiropentane[41] are, respectively, 48.0 ± 0.4 and 44.2 ± 0.2 kcal/mol. Hence the $\Delta H°$ for the cyclopropanation step is −106.3 ± 0.7 kcal/mol. As a theoretical benchmark, the value was calculated at the W1 level.[42] It afforded a $\Delta H°$ of −105.0 kcal/mol. The $\Delta H°$ values derived from the other computational models employed here were −114.9 kcal/mol for CASPT2-g3 (using a "supermolecule" consisting of $CH_2$ and methylenecyclopropane separated by 20 Å to calculate the enthalpy of the reactants), −102.8 for RCCSD(T), and −102.0 for CR-CC(2,3). The broken-symmetry UCCSD(T) results were identical to those for RCCSD(T) because the unrestricted calculations converged on the restricted result as the lowest-energy solution in each case.

**Stereomutation of Spiropentane.** The stereomutation of spiropentane has been thoroughly analyzed by Johnson and coworkers using a CASPT2 computational model.[43] Experimentally, it is known that spiropentane-*cis*-1,2-$d_2$ interconverts with the *trans* isomer and that this takes place faster than isomerization to methylenecyclobutane.[44] However, this observation does not reveal the details of how the stereomutation occurs. The situation is summarized in Scheme 2. The *cis*−*trans* isomerization might occur by a monorotation pathway. It cannot be achieved by disrotation alone, or by conrotation alone, but it could be accomplished by conrotatory opening and disrotatory closure or vice versa. Microscopic reversibility guarantees that these mixed-mode double rotations will face an overall barrier equal to that for the higher energy of the conrotation−conrotation or disrotation−disrotation pathways but cannot provide information about the preference between double- and single-rotation mechanisms. The calculations of Johnson et al. found a very small (0.1 kcal/mol) preference for monorotation. They calculated[43] an overall activation enthalpy of 51.3 kcal/mol, in excellent agreement with the experimental value of 50.9 ± 1.0 kcal/mol.[44]

The stereomutation reaction turns out to provide a very severe test for the single-reference computational models, as shown in Table 1. The result that stands out as a spectacular error is the activation enthalpy for monorotation at the RCCSD(T) level. It is easy to understand why this occurs. The monorotation transition structure found by optimization at the BS-UCCSD/cc-pVDZ level has $C_s$ symmetry and corresponds to a ground state of $A''$ symmetry (Figure 1). However, the RHF reference used in the RCCSD(T) calculations is obviously forced to be of $A'$ symmetry, implying that it makes zero contribution to the ground-state wave function. The barrier to monorotation calculated by the CR-CC(2,3) model is also too high but not as badly in error as that from the RCCSD(T) estimate. Somewhat surprisingly, the CR-CC(2,3) model apparently describes the disrotation TS rather poorly, even though it does not suffer from the symmetry problem outlined for the monorotation TS.

**TABLE 1: Calculated Enthalpies (kcal/mol) Relative to Spiropentane[a]**

| Structure | RCCSD(T) | BS-UCCSD(T) | CR-CC(2,3) | CASPT2-g3 |
|---|---|---|---|---|
| conrotation TS | 47.9 | 48.2 | 50.0 | 48.1 |
| disrotation TS | 52.4 | 49.4 | 62.3 | 52.1 |
| monorotation TS | 115.5 | 51.4 | 61.4 | 51.9 |
| biradical intermediate | 52.3 | 46.7 | 55.8 | — |

[a] Basis sets and levels of theory used for geometry optimization are described in the text.

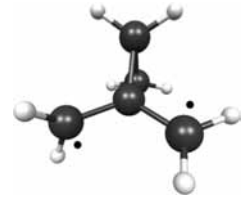


**Figure 1.** Geometry of the $C_s$ symmetry transition structure for monorotatory stereomutation of spiropentane, from BS-UCCSD/cc-pVDZ calculations.

Both the CASPT2-g3 and BS-UCCSD(T) models seem to do a good job of describing all three stereomutation pathways, although they differ in detail. The BS-UCCSD(T) calculation favors a disrotation/conrotation route for *cis*−*trans* isomerization of spiropentane-*cis*-1,2-$d_2$ and predicts an activation enthalpy of 49.4 kcal/mol. It finds the $C_{2v}$ biradical to be an intermediate with an enthalpic barrier of 1.5 kcal/mol to conrotatory closure. The CASPT2-g3 calculation very slightly favors the monorotation route for *cis*−*trans* isomerization and predicts an activation enthalpy of 51.9 kcal/mol. The CASSCF(12,12)/cc-pVDZ geometry optimizations do not find any biradical intermediates along the stereomutation coordinates. Instead, there are three different transition structures, one of $C_1$ and two of $C_s$ symmetry. The $C_1$ structure is the TS for monorotation; it deviates from $C_s$ symmetry by slight pyramidalization at the acyclic methylenes. The lower energy of the two $C_s$ structures is, somewhat surprisingly, the TS for conrotation (confirmed by an IRC calculation); the other is the TS for disrotation. Presumably, there exists a valley-ridge inflection between these two, but no attempt has been made to locate it.

**Isomerization of Spiropentane to Methylenecyclobutane.** A great deal of experimental work has been done on the stereochemistry of rearrangement of various substituted spiropentanes to the corresponding methylenecyclobutanes.[45−49] The upshot is that the reaction shows some stereoselectivity but not complete stereospecificity. This result has been interpreted as evidence for a competition between stepwise and concerted pericyclic mechanisms for the reaction.[48] One of the aims of

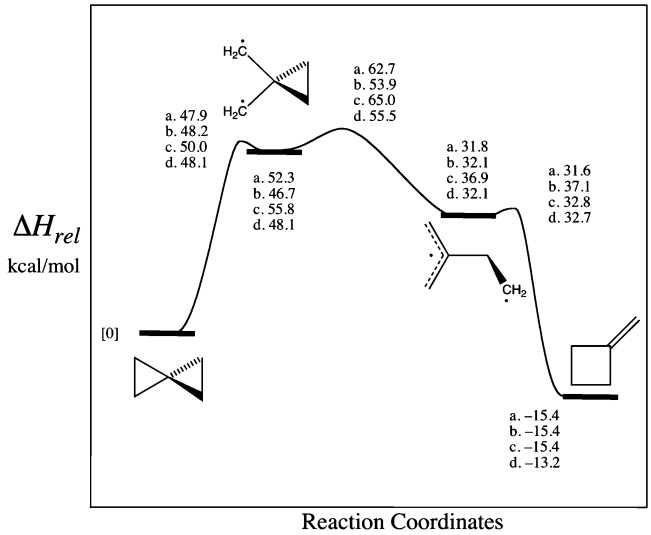



**Figure 2.** Summary of computed enthalpy differences between stationary points along the coordinates for spiropentane to methylenecyclobutane rearrangement. The figures refer to: a. RCCSD(T), b. BS-UCCSD(T), c. CR-CC(2,3), d. CASPT2-g3. Other details of the calculations are provided in the text.

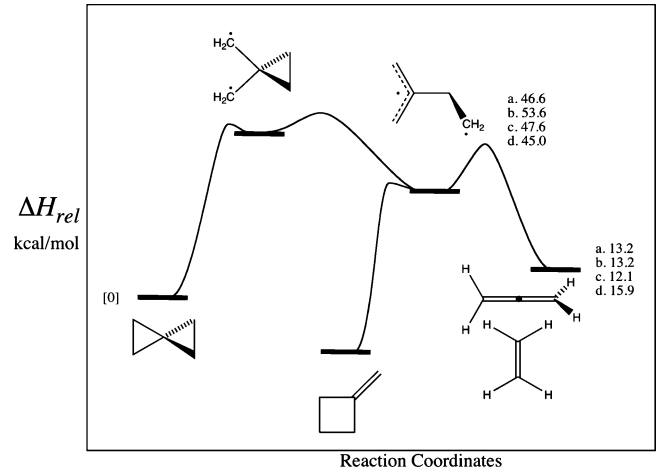



**Figure 3.** Summary of computed enthalpy differences between stationary points along the coordinates for spiropentane and methylenecyclobutane fragmentation. The figures refer to: a. RCCSD(T), b. BS-UCCSD(T), c. CR-CC(2,3), d. CASPT2-g3. Other details of the calculations are provided in the text.

the present calculations was to find out whether there was evidence for such a mechanistic description. In brief, the answer is "no". As it turns out, the characterization of the reaction as either stepwise or concerted is not straightforward and probably not even very useful.

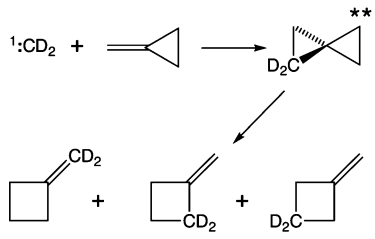
The BS-UCCD and CASSCF geometry optimizations both found a well-defined biradical intermediate and transition structures linking it to methylenecyclobutane and to the biradical involved in spiropentane stereomutation. However, the higher-level single-point calculations differed on whether there was a barrier to closure of the biradical to methylenecyclobutane. As can be seen from Figure 2, the four computational models that were applied to each stationary point differed considerably in their assessment of relative energies. However, they agreed on one important point, which allowed their accuracy to be judged against experiment. It was that the rate-limiting transition state was the one between the two biradicals. Consequently, the difference between its enthalpy and that of spiropentane should define the activation enthalpy for the spiropentane to methylenecyclobutane rearrangement, for which the experimental value is 56.3 kcal/mol.[8] By this metric, the CASPT2-g3 model is the most accurate, with the BS-UCCSD(T) also quite close. The RCCSD(T) and CR-CC(2,3) calculations gave barriers for the rearrangement that were substantially too high.

The BS-UCCSD(T) model leads to a description of the spiropentane to methylenecyclobutane isomerization as a stepwise reaction with well-defined biradical intermediates, being protected from the local minima on the potential energy surface by barriers. However, the description is more problematic for the other three models. They find no barrier for conrotatory closure of one biradical to spiropentane and little or no barrier for closure of the other biradical to methylenecyclobutane. One might, therefore, choose to characterize their description of the isomerization as single step, but it could hardly be called "concerted," and it definitely is not "pericyclic" because there is no transition structure involving a cyclic array of overlapping orbitals for making and breaking bonds.

It seems almost certain that the spiropentane to methylenecyclobutane rearrangement is one in which reaction dynamics play an important role in determining the overall stereochemistry.[50] Simulation of the reaction by MD calculation should be possible. Preliminary results using a BS-UDFT model suggest that by starting trajectories in the vicinity of the rate-limiting transition structure, and then running them forward to methylenecyclobutane and backward to spiropentane, one can map out the overall stereochemistry. It would be interesting to see how the predicted stereochemistry depends on the electronic-structure model used to describe the PE surface, and which simulation best fits the experimental facts. Calculations of this kind are planned for the near future.

**Fragmentations of Spiropentane and Methylenecyclobutane to Allene + Ethylene.** At sufficiently high temperatures,[8,51] or with the vibrational energy available from chemical activation,[7] both spiropentane and methylenecyclobutane will fragment to allene and ethylene. It is not clear from the experiments how these fragmentations and the interconversion of spiropentane and methylenecyclobutane might be linked on the PE surface, but the present calculations come to a consistent conclusion on that point. All of the computational models explored in this study suggest a mechanism in which the allylic biradical involved in the isomerization (see Figure 3) has an alternative pathway with a higher barrier, leading to fragmentation. The experimental activation enthalpy for methylenecyclobutane fragmentation to allene + ethylene is 62.1 kcal/mol.[51] That datum places the transition state 46.9 kcal/mol above spiropentane. As shown in Figure 3, the RCCSD(T) calculations do quite well in matching the experimental result, and in fact, all of the models except BS-UCCSD(T) are reasonably good. The failure of the broken-symmetry coupled-cluster calculations is interesting and initially surprising because one might expect the BS-UCCSD(T) calculations to converge on the RCCSD(T) result if it represented the best available solution. However, what happens is a crossover in relative energies of the restricted and broken-symmetry, unrestricted wave functions. At the reference Hartree−Fock level, the unrestricted wave function is lower in energy, presumably because it can give an approximate correction for nondynamic electron correlation. However, after the coupled-cluster expansion, the restricted solution is lower in energy, perhaps implying that the contribution from nondynamic correlation is not large enough to invalidate a single-reference calculation (and also implying that the RHF reference function is superior under those circumstances). In support of this assessment, it may be noted that the $T_1$ diagnostic was found to

**SCHEME 3: Comparison of Observed Product Distribution in the Experiment of Doering et al. with Those Calculated on the Basis of Equilibrium Isotope Effects (EIE) at 298 and 600 K[a]**




| | | | |
|---|---|---|---|
| Expt.: | 19% | 54% | 27% |
| 298 K EIE: | 21% | 51% | 28% |
| 600 K EIE: | 24% | 50% | 26% |

[a] Calculations were carried out at the CCSD/cc-pVDZ level.

have a value of 0.0152, i.e., below the 0.02 threshold generally considered to mark the boundary of reliability for single-reference coupled-cluster calculations.[52] A similar crossover occurs for other structures on this PE surface, as discussed in more detail in the concluding section of this paper.

**Equilibrium Isotope Effects for Isomers of Methylenecyclobutane-$d_2$.** As discussed in the Introduction, the experiments of Doering and co-workers on addition of $CD_2$ to methylenecyclopropane led them to conclude that the rearrangement of the chemically activated spiropentane-$d_2$ primary product occurred slower than IVR, in accord with the assumption underlying statistical kinetic models such as RRKM theory. However, interpretation of their data is hampered by several uncertainties. As described above, it seems likely that the methylenecyclobutane secondary products could themselves be produced in a chemically activated state. If so, the isotopic isomers could interconvert and thereby obscure the information about their initial ratio, which is where any signs of incomplete IVR might be found. Complete equilibration of the three isotopic isomers of geminally labeled methylenecyclobutane-$d_2$ would result in a ratio that differed from 1:2:1 as a result of equilibrium isotope effects. Since the present calculations allowed easy evaluation of those isotope effects, the results are included in this paper. The principal uncertainty concerns the effective temperature at which the effects should be computed. One could argue that the chemical activation resulting from the cyclopropanation of methylenecyclopropane results in the products having an effective temperature considerably above that at which the experiment was conducted. However, it is not clear that the vibrational excitation of products resulting from chemical activation corresponds to a true temperature or, if it does, what that temperature may be. In the absence of a clear-cut solution to this problem, the equilibrium isotope effects were calculated at two different temperatures: 298 K, corresponding to the ambient temperature, and 600 K, selected as a temperature at which the thermal rearrangement of spiropentane to methylenecyclobutane occurs at a reasonable rate. The results are summarized in Scheme 3.

Because of the unresolved issues surrounding the effect of chemical activation on the isotope effects and because of the lack of information about uncertainties in the experimental product ratios, one cannot make a definitive conclusion from the data summarized in Scheme 3. Nevertheless, the calculations suggest that one should not rule out the possibility that the methylenecyclobutane generated in the experiment of Doering and co-workers was chemically activated and that this allowed the isotopic isomers to interconvert, reaching a final ratio determined by equilibrium isotope effects. Obviously, if that were the case, any information about rates of IVR following the cyclopropanation step would be lost, and the apparent disagreement with the results of Rynbrandt and Rabinovitch would become moot.

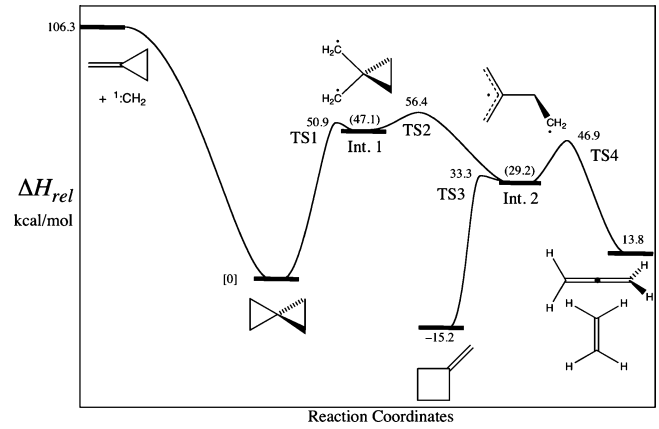



**Figure 4.** Summary of connections between stationary points deduced from the present work. Enthalpies relative to spiropentane are experimental except for those of the two biradical intermediates, which come from MkCCSD(T)/cc-pVTZ//CASSCF(12,12)/cc-pVDZ calculations.

## Conclusions

Many of the conclusions from the present calculations are conveniently summarized by reference to Figure 4. It summarizes the connections between stationary points that have been deduced from the calculations.

The first statement about the mechanism that can be made is that there is no evidence for a concerted pericyclic reaction at any stage (excluding the initial cyclopropanation). If that assertion is correct, then the stereoselectivities that have been observed for some steps of the overall reaction[48] probably arise from dynamical effects,[50] which could be (and are planned to be) probed by MD simulations. The second point to be made is that if the methylenecyclobutane generated by $CH_2$ addition to methylenecyclopropane is initially formed with chemical activation sufficient to promote subsequent fragmentation to allene and ethylene, as Frey and co-workers have suggested,[7] then the fact that the barrier for degenerate rearrangement is 13 or more kcal/mol below that for fragmentation suggests that chemically activated rearrangement is also likely to occur. If it does, then looking for signs of incomplete IVR through label distributions in the methylenecyclobutane, as Doering and co-workers attempted to do,[3] could be difficult. An alternative strategy of looking at label distributions in the fragmentation products might be more promising because the barriers to stereochemical isomerization of allene and ethylene are high and the excess vibrational energy in each fragment would be lower than in methylenecyclobutane.

The second general goal of this study was to compare computational models for dealing with reactions that involve intermediates in which significant nondynamic electron correlation can be anticipated. Table 2 summarizes the outcome; relative enthalpies (with spiropentane defined as zero) are compared with experiment or, in the case of the two biradical intermediates, with the results of MkCCSD(T) calculations.

Several comments about the interpretation of the data in Table 2 are probably in order. The first concerns the comparison of theory with experiment for TS1. As described above, the experimental value refers to the activation enthalpy for *cis*/*trans*

**TABLE 2: Summary of Relative Enthalpies in kcal/mol for the Stationary Points Identified in Figure [4,a]**

| structure | RCCSD(T) | BS-UCCSD(T) | R/U-CCSD(T) | CR-CC(2,3) | CASPT2-g3 | exptl |
|---|---|---|---|---|---|---|
| $CH_2$ + MCP | 102.8 | 102.8 | 102.8 | 102.0 | 114.9 | 106.3 |
| spiropentane | [0] | [0] | [0] | [0] | [0] | [0] |
| TS1 | 52.4 | 49.4 | 49.4 | 61.4 | 51.9 | 50.9 |
| Int. 1 | 52.3 | 46.7 | 46.7 | 55.8 | 48.1[b] | 47.1[c] |
| TS 2 | 62.7 | 53.9 | 53.9 | 65.0 | 55.5 | 56.4 |
| Int. 2 | 31.8 | 32.1 | 31.8 | 36.9 | 32.1 | 29.2[c] |
| TS 3 | 31.6 | 37.1 | 31.6 | 32.8 | 32.7 | 33.3 |
| MCB | −15.4 | −15.4 | −15.4 | −15.4 | −13.2 | −15.2 |
| TS 4 | 46.6 | 53.6 | 46.6 | 47.6 | 45.0 | 46.9 |
| $C_3H_4$ + $C_2H_4$ | 13.2 | 13.2 | 13.2 | 12.1 | 15.9 | 13.8 |
| rms error | 3.2 | 3.1 | 1.9 | 6.2 | 3.3 | |

[a] MCP and MCB are, respectively, methylenecyclopropane and methylenecyclobutane. See text for explanation of the column labeled R/U-CCSD(T). [b] This value is for the conotatory transition structure because the CASSCF geometry optimization did not find "Int. 1" to be a local minimum. [c] Relative enthalpies from MkCCSD(T) calculation rather than experiment.

isomerization of spiropentane-1,2-$d_2$. However, that reaction cannot be accomplished by following the lowest-barrier route for formation and reclosure of the biradical labeled Int. 1 in Figure 4, which all of the computational models find to be conrotatory double rotation. Hence, the theoretical entries for this row of Table 2 correspond to the lowest barrier routes for the observed reaction, which some models find to be monorotation and others find to be a mixed conrotation/disrotation mechanism. Although necessitated by the nature of the available experimental information, this treatment of the stereomutation results makes the overall performance of the RCCSD(T) calculations, as judged by the rms error, look much better than it really is. If there had been a way to include the RCCSD(T) result for the monorotatory stereomutation, the RCCSD(T) model would have fallen to the bottom in the ranking for overall accuracy.

The second comment in Table 2 concerns the MkCCSD(T) relative enthalpy for Int. 1, entered in the column labeled "exptl". The MkCCSD(T) calculations were based on CASSCF(12,12)/cc-pVDZ geometries. However, the CASSCF calculations did not find a local minimum along the stereomutation coordinate for spiropentane. Consequently, the MkCCSD(T) calculations were carried out on the CASSCF transition structure for conrotation.

The feature of Table 2 requiring most comment is the column labeled R/U-CCSD(T). The data in this column represent a composite of the results from the two columns to its left. As described earlier, the coupled-cluster calculations on TS4 showed a crossover phenomenon, in which the broken-symmetry unrestricted result was of lower energy for the Hartree−Fock reference wave function, but the restricted solution was of lower energy at the CCSD(T) level. A similar crossover occurred for the conrotatory ring-opening transition structure of spiropentane, as well as for the stationary points labeled Int. 2 and TS3 in Figure 4. The data in the R/U-CCSD(T) column of Table 2 arise from selection of the lower absolute energy result from the RCCSD(T) and BS-UCCSD(T) calculations for each stationary point. Such a selection is not strictly defensible since coupled-cluster methods are not variational; on the other hand, it is certainly striking that this procedure gives the best match to experiment and the MkCCSD(T) results of any of the models investigated. It would be interesting to see whether a similar approach works well for other reactions involving singlet biradicals.

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**Supporting Information Available:** Full literature citations for refs 14, 15, 17, and 23. Cartesian coordinates and energies of all stationary points. This material is available free of charge via the Internet at http://pubs.acs.org.

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