notable discrepancies are still present. It would be of interest to compare MFP results for the dimethylthiiranes.

The Cope Rearrangement Revisited

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Abstract: Using a CASSCF wave function and a 6-31G* basis set we have located several stationary points on the potential energy surface for the Cope rearrangement. At this level of theory we find both a synchronous path through a symmetrical aromatic transition state and a non-concerted path through a disymmetrical transition state followed by a symmetrical biradicaloid intermediate. After zero-point and thermal corrections both paths appear possible. A more elaborate description of electron correlation does not yield a clear preference for either path.

I. Introduction

Synchronicity and concertedness in the vicinity of the transition states in the Cope rearrangement, and the structure of these transition states, continue to be the subject of intense debate. A review of the present state of knowledge on this problem has recently been published.[1] In this discussion we will follow Dewar's definition that "concerted" implies a one-step mechanism with no stable intermediate while "non-concerted" implies a multiple-barrier reaction path with at least one stable intermediate. Unfortunately, for a nearly flat potential energy surface a calculated reaction mechanism can change between concerted and non-concerted as the quality of the theory is changed. For a concerted path Dewar defines "synchronous" as one where all bonding changes have taken place to a more-or-less equal extent and "non-synchronous" as one where some changes are much more complete than others. "Synchronicity" is only loosely defined. It is unclear what CC bond length would correspond to a "half-broken" bond. Also, at a symmetrical transition state, the reaction coordinate (the normal mode of imaginary frequency) will necessarily make equal and opposite changes in the equivalent forming and breaking bonds so all concerted reactions with identical reactants and products will be locally synchronous.

For the Cope rearrangement, the C_3–C_4 bond length and the number of imaginary frequencies at the midpoint of the reaction are indications of concertedness and synchronicity. This interallylic CC bond length in the chair and boat conformations of the transition-state region is also the key parameter which reflects the biradical or aromatic character of the structures involved in the rearrangement. Additionally, orbital occupation numbers are sometimes discussed.

Some recent attempts to resolve the discrepancy between semiempirical[2,3] and ab initio studies[4-7] have used perturbation and configuration interaction methods based on self-consistent-field (SCF) orbitals. The sensitivity of the optimized structures to the level of theory used[4] suggests that the bias introduced by using SCF orbitals is very difficult to overcome. This is of paramount importance, of course, since the key issue in this problem is the amount of biradical character in the transition structures.

In this respect the ab initio study by Dewar and Healy[6] is seriously flawed. They attempted to use closed-shell SCF followed by MPn to calculate the relative energy of the aromatic and biradicaloid structures. But for true biradicaloids, like H_2 at large internuclear distances, this procedure fails. A more correct, but still dubious, procedure is to use UHF with a broken symmetry wave function followed by UMPn. It is no wonder that Dewar was unable to find a biradicaloid structure with a RHF wave function.

In this paper, we report calculations which follow the more desirable approach of Osamura et al.[4] and Morokuma et al. (MBH).[5] They are based on a multiconfiguration SCF (MCSCF) form of the wave function which has enough flexibility to take into account the most significant electron correlation effects associated with bond breaking and bond formation in the rearrangement. However, the present study goes beyond the work of these researchers in the use of a polarized basis set throughout. As will become clear later, this larger basis set yields significantly different relative energies, compared to the results of MBH. Seven stationary points on the potential energy surface have been characterized, including three genuine transition states and two stable intermediates with comparable energies. The role of these species in the rearrangement has been investigated by characterizing the intrinsic reaction coordinate (IRC). One of the two stable intermediate structures determined in this work has not been characterized previously, to the best of our knowledge. Also, one of the transition states has not been found before in ab initio calculations.

II. Overview of Results

A total of seven stationary points on the potential surface were characterized with MCSCF (6-31G*) wave functions and are depicted in Figure 1. They are the following: (1) the allyl + allyl structure, whose energy is used as a reference; (2) a loose boat transition state with an interallylic distance $R = 2.615$ Å,

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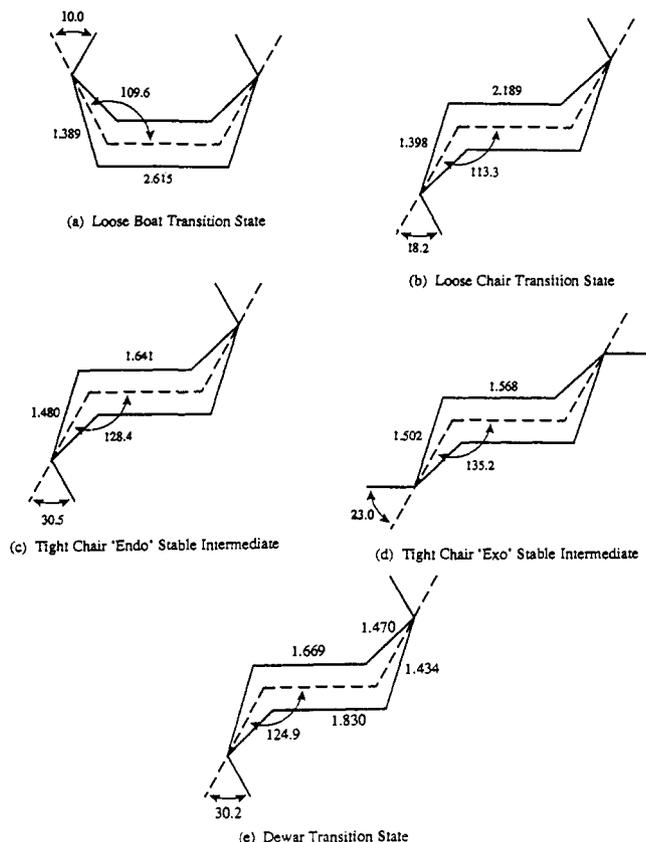
Figure 1. Stationary points for the Cope rearrangement from a CASSCF calculation with a 6-31G* basis set.

Figure 2. Paths connecting stationary points for the Cope rearrangement.

an imaginary frequency of 406 cm^{-1} corresponding to the asymmetric stretch of the interallylic CC bonds, and a relative energy of -1.7 kcal/mol; (3) a loose chair transition state with an interallylic distance $R = 2.189$ Å, an imaginary frequency of 779 cm^{-1} corresponding to the asymmetric stretch of the interallylic CC bonds, and a relative energy of -6.3 kcal/mol; (4) a 1,5-hexadiene structure as the product on the reaction coordinate passing through the loose chair transition state, with a relative energy of -54.0 kcal/mol, 47.7 kcal/mol more stable than the loose chair transition structure; (5) a tight chair stable intermediate with relative energy of -8.1 kcal/mol where the CH bonds are "endo" with respect to the 2- and 5-C atoms and the interallylic distance is $R = 1.641$ Å; (6) a second tight chair stable intermediate with relative energy of -4.8 kcal/mol where the CH bonds are "exo" with respect to the 2- and 5-C atoms and the interallylic distance is $R = 1.568$ Å; and (7) an unsymmetrical "Dewar" transition state with interallylic bond lengths of 1.67 and 1.83 Å, with an imaginary frequency of 598 cm^{-1} and a relative energy of -6.9 kcal/mol.

The loose boat and loose chair transition structures and the "endo" tight chair stable intermediate structures are similar to the structures reported by MBH. The main difference with their work resides in our relative energy of the tight chair structure being 1.9 kcal/mol more stable than the loose chair transition state, in contrast with being 22 kcal/mol less stable in the work of MBH. This tight chair structure is found to be 8.1 kcal/mol more stable than two allyl radicals, compared to being described as 8.6 kcal/mol less stable in the work of MBH. The differences between MBH's methods and ours are only a somewhat better split-valence quality basis set and d-type polarization functions on the carbon atoms.

The longer interallylic distances in both the loose boat and loose chair transition states, compared to the structures given by MBH, can be explained on the basis of the larger calculated stabilization energy of 1,5-hexadiene (47.7 kcal/mol compared to 40.7 kcal/mol for MBH). In accord with Hammond's postulate,[8] the transition
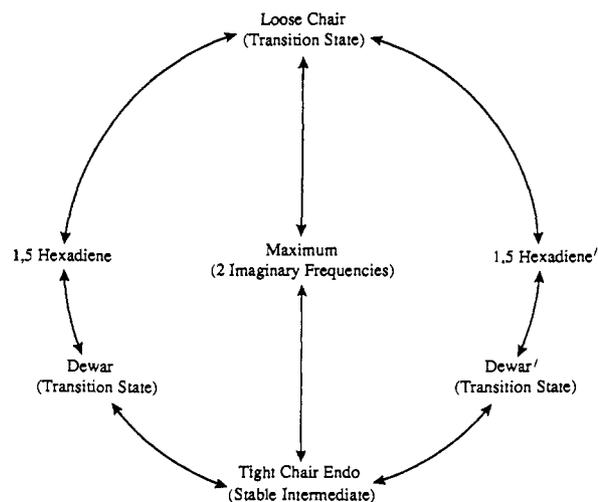
state is earlier along an allyl dimerization reaction coordinate, and thus the interallylic distance is longer.

Our finding of a tight chair stable intermediate with energy 1.9 kcal/mol below the loose chair transition state is in accord with the AM1 results of Dewar et al.[2,3] as far as the relative energies of these species is concerned. Both the loose chair transition state and the tight chair stable intermediate have C_{2h} symmetry. Starting from the loose chair transition state, we determined the intrinsic reaction coordinate pathway[9,10] and showed that it leads to 1,5-hexadiene. The tight chair does not belong to this IRC. Analysis of the shortening of one interallylic CC bond and of the lengthening of the other interallylic CC bond shows clearly that the magnitude of the changes for these two processes is nearly equal over a range that covers almost one-third of the reaction pathway. This finding establishes firmly that this reaction path is synchronous. Additionally it can be noted that the C_3-C_4 distance in the transition state corresponds roughly to the bond length for half dissociating a C–C bond, and the other bond lengths are near those expected for a π bond order of $^1/_2$.

We also found the "Dewar" transition state on a path from the tight chair intermediate to the diene. Additionally, we examined the bond isomerization barrier between the tight chair intermediate and loose chair transition state along a C_{2h} cut in the potential surface. This stationary point was only 1 kcal/mol higher in energy, but it had two imaginary frequencies. The paths connecting these various stationary points are depicted symbolically in Figure 2 for easy reference.

III. Computational Results

The MCSCF wave function used to describe the reactants, transition states, and products of the rearrangement was designed on the basis of our chemical understanding of the reactive process. In 1,5-hexadiene, we consider the six electrons which form the 1–2 C=C π bond, the 5–6 C=C π bond, and the 3–4 C—C σ bond. With each of these three electron pairs, we associate a bonding and an antibonding orbital, for a total of six molecular orbitals. In the rearrangement, the electrons of the π bonds unpair and two electrons from one pair each recouple to form the 1–6 C—C σ bond synchronously with the unpairing of the electrons of the 3–4 C—C σ bond. In the process, the terminal CH$_2$ groups undergo rotation and bending. The MCSCF wave function is a complete active space SCF (CASSCF) wave function obtained by distributing the six active electrons among the six active orbitals in all ways consistent with spin and spatial symmetry. As the reaction proceeds, the MCSCF wave function adjusts smoothly to bond breaking and bond formation to describe the reactants, transition states, and products in a consistent fashion. Of course,

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Table I. Changes in the Interallylic C_3–C_4 and C_1–C_5 Bond Distances Along the IRC Starting from the Loose Chair TST

point	$-\Delta E$, kcal/mol	ΔR_{34},[a] Å	ΔR_{16}, Å
1	0.0	0.000	0.000
2	0.5	−0.040	0.039
3	0.9	−0.052	0.051
4	1.6	−0.071	0.069
5	3.0	−0.100	0.095
6	5.4	−0.141	0.131
7	7.7	−0.177	0.159
8	10.7	−0.219	0.191
9	15.2	−0.281	0.236
10	21.0	−0.364	0.296
product	47.7	−0.616	1.851

[a] At the transition state, $R_{34} = R_{16} = 2.189$ Å.

the electron correlation effects accounted for by the MCSCF wave function vary from reactant to transition state to product. The MCSCF results are, at best, of semiquantitative accuracy. Improved accuracy requires a more extended treatment of electron correlation effects beyond those described by the MCSCF wave function as described in a later section of this paper.

The optimized structures of the various species are shown in Figure 1, and the relative energies are given in Table II. The calculations were performed with the 6-31G* basis set,[11] using the HONDO program.[12,13] The nature of the stationary points on the potential energy surface was characterized by complete vibrational analysis. As indicated earlier, the loose boat and loose chair structures are genuine transition states. The chair structure has 2.5 kcal/mol more zero-point vibrational energy than the boat structure. The "endo" and "exo" tight chair structures are stable intermediates with nearly equal zero-point energy. The zero-point energy of the intermediates is about 2.2 kcal/mol larger than that for the chair transition state.

From a wave function point of view, it is useful to consider the occupation number of the weakly occupied molecular orbitals of the MCSCF wave functions as an indication of the biradical character of the species. The reference point is 1,5-hexadiene with a total of 0.20 electron in the three least occupied MCSCF orbitals. In the loose chair transition state, there is 0.30 electron in the weakly occupied orbitals, and in the loose boat, there is 0.48 such electron. This difference can be attributed to the longer interallylic bond distance in the loose boat caused by greater steric repulsion, and the fractionally occupied orbitals are localized on carbons 1, 3, 4, and 6. By contrast, the tight chair exo intermediate has 0.93 electron in these orbitals which is consistent with its description as a diyl. The lower energy endo tight chair intermediate has only 0.62 electron in these orbitals because of favorable through bond interactions which splits the degeneracy of the symmetric and antisymmetric combination of the lone electron orbitals localized on C_2 and C_5 and reduces its biradical character.

As indicated earlier, the IRC pathway for the Cope rearrangement originating from the loose chair transition state does not pass through either of the tight chair stable intermediates but rather leads directly to the product 1,5-hexadiene. Similarly we found that the IRC originating from the loose boat transition state does not pass through the stable intermediates. We note that in the tight chair "endo" biradicaloid intermediate, the lowest frequency mode involves torsion of the carbon ring at a harmonic frequency of 216 cm^{-1}. The symmetric CC stretch of the interallylic bonds has a frequency of 608 cm^{-1}, while the frequency of the asymmetric interallylic CC stretch is 706 cm^{-1}. For the tight chair "exo" intermediate, the lowest frequency, 186 cm^{-1}, corresponds to torsion of the carbon ring, the interallylic symmetric CC stretch is at 836 cm^{-1}, and the asymmetric stretch is at 885 cm^{-1}. Although we did not follow it, the IRC starting from the

low-frequency mode of the "endo" intermediate is of a form to lead smoothly to the "Dewar" transition state.

After corrections for vibration, the calculated relative enthalpy of 1,5-hexadiene compared to two non-interacting allyl radicals is 48.0 kcal/mol, which compares favorably with the experimental enthalpy change[12] of 57.0 kcal/mol. The calculated activation barrier for the chair transition state of 47.7 kcal/mol may be corrected for zero-point energy, yielding an enthalpy of activation, $\Delta H(298)$, of 46.0 kcal/mol, to be compared with the experimental value of 33.5 kcal/mol.[13]

IV. CI Calculations

The MCSCF method can be relied upon to give a good qualitative description of the structures important in the Cope rearrangement. However, it gives only a semiquantitative estimate of the energy differences between these structures. We have used multireference configuration interaction (MRCI) and quaside-generate variational perturbation theory[14] (QDVARPT) to improve the description of the dynamical correlation in the molecules. The multireference analogue of the Davidson correction was used to correct the CI results for the effect of quadruples, while QDVARPT is nearly size consistent and requires no further correction. The calculations were performed at the MCSCF optimized geometries.

The reference configurations were selected iteratively until all configurations with a weight greater than 0.02 in the MRCI wave function were included in the reference space. This led to between 15 and 20 reference configurations for the structures. Two sets of calculations were performed. The first set correlated only the 6 electrons which were contained in the active space of the MCSCF calculations, while the second set correlated all 34 valence electrons. All single and double excitations from the reference space were considered. Perturbation theory was used to reduce the number of configurations included in the CI matrix, and also to estimate the contribution to the final answer of the neglected configurations. In all cases, the threshold for leaving out configurations was arranged so that fewer than 65 000 configurations were explicitly treated in the CI matrix. Truncation of the CI expansion requires a good choice for the orbitals. We used the MCSCF natural orbitals for those orbitals included in the MCSCF active space; K orbitals[15] generated from these natural orbitals were used for the other virtual orbitals.

Table II contains the results of the calculations together with the original MCSCF results. The table also contains the difference between the energy of the allyl supermolecule and twice the energy obtained from equivalent but more accurate calculations on the allyl monomer. The absolute value of this quantity is a measure of the reliability of our computed total energies. Of course, since the molecules considered are very similar, it is to be expected that our differential energies will be more accurate than this. It can be seen that the 34 electron calculations are not consistent. One reason for this is the extrapolation procedure used to estimate the effect of neglected configurations in the CI expansion. For example, the extrapolation for the QDVARPT calculation on the diallyl supermolecule accounts for over 80 kcal/mol.

In contrast, the extrapolated 6 electron QDVARPT calculations appear to be consistent and we regard these as our best results. All structures are stabilized with respect to the diallyl supermolecule in going from the MCSCF results to the QDVARPT results. The loose chair and Dewar structure are both stabilized relative to 1,5-hexadiene leading to a reduction in the calculated activation energy for the Cope rearrangement through either of these transition states. One indication of possible sources of error in the energy differences from the 6 electron calculations can be gleaned from the 34 electron calculations where, in the case of the two tight chair stable intermediates, some configurations which were not included in the 6 electron calculations had to be put into the reference space of the larger calculations. The two configurations in question possessed weights of just over 0.02, had four

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Table II. Energies of Structures Important in the Cope Rearrangement

structure	MCSCF energy	6 electron CI energy (extrap.)	6 electron QDVARPT (extrap.)	34 electron CI energy (extrap.)	34 electron QDVARPT (extrap.)
diallyl supermolecule	−232.96716	−232.98457 (−232.9864)	−232.98743 (−232.9864)	−233.50535 (−233.7552)	−233.61650 (−233.7376)
tight chair exo	−4.8	−8.6 (−9)	−8.7 (−9)	−7.8 (+5)	−3.9 (+3)
loose chair	−6.3	−12.4 (−13)	−12.6 (−13)	−20.6 (−32)	−31.1 (−32)
loose boat	−1.7	−5.2 (−6)	−5.3 (−6)	−5.4 (−36)	−13.8 (−31)
tight chair endo	−8.2	−13.9 (−14)	−14 (−14)	+2.2 (+1)	+7.6 (+3)
hexadiene	−54.0	−56.9 (−58)	−56.9 (−58)		
Dewar structure	−6.9	−12.6 (−14)	−12.8 (−14)		
2-(allyl monomer)	0.00	−1.5 (−0.5)	−1.4 (−0.5)	−83.3 (+27)	−57.6 (+10)

a The absolute energy of the diallyl supermolecule is given in hartrees. All other energies are in kcal/mol relative to the diallyl supermolecule. Where appropriate, extrapolated energies are given in parentheses underneath the unextrapolated quantities.

Table III. Thermodynamic Quantities for Important Structures in the Cope Rearrangement*a*

structure	ΔE_e	ΔE_0	$\Delta H(500)$	$S(500)$	$\Delta F(500)$
diallyl supermolecule	0.0	0.0	0.0	138.8	0.0
tight chair exo	−8.8	−0.7	−3.1	90.7	+20.9
loose chair	−13.0	−6.9	−9.0	92.2	+14.3
loose boat	−6.0	−2.5	−3.4	98.6	+16.7
tight chair endo	−14.4	−6.1	−8.6	89.2	+16.2
hexadiene	−57.7	−50.6	−51.8	100.0	−32.4
Dewar structure	−14.4	−6.8	−9.8	87.8	+15.7

a Absolute entropies are given in cal/(mol·K⁻¹). The energies are in kcal/mol relative to the diallyl supermolecule and they were derived from the extrapolated QDVARPT 6 electron calculation. Zero point and thermodynamic corrections are based on CASSCF structures and vibrational frequencies.

singly occupied orbitals, and corresponded to a $\pi\sigma \rightarrow \pi^*\sigma^*$ excitation.

Table III contains thermodynamic information obtained from calculations of the partition functions with our ab initio results. The extrapolated 6 electron QDVARPT results are used as a base for the thermodynamic quantities. Zero-point corrections are obtained from the MCSCF frequencies; the zero-point correction for the allyl supermolecule is 86.7 kcal/mol. As expected, the corrections favor the transition states with respect to the minima. The entropy is least for the tight chair species and greatest for the diallyl system as would also be expected from simple arguments. Because the entropy is computed for a local harmonic oscillator model, it will be underestimated for 1,5-hexadiene relative to the other species by the entropy associated with internal rotation. A better estimate[16] is probably 107 cal/(mol·K⁻¹) at 500 K for the entropy of 1,5-hexadiene.

After correction for vibration, the calculated relative enthalpy of 1,5-hexadiene compared to two non-interacting allyl radicals is 51.8 kcal/mol, which compares favorably with the experimental enthalpy change[17] of 57.0 kcal/mol. The calculated activation barrier for the chair transition state of 44.7 kcal/mol may be corrected for zero-point energy, yielding an enthalpy of activation,

$\Delta H(298)$, of 43.0 kcal/mol, to be compared with the experimental value of 33.5 kcal/mol.[18]

V. Conclusions

The MCSCF calculations presented here find a synchronous reaction path for the Cope rearrangement in agreement with other ab initio calculations. This path contains a symmetrical chair transition state with an "aromatic" wave function. At the same time, we find symmetrical biradicaloid stable intermediates of the chair form with unsymmetrical transition states, in agreement with semiempirical results of Dewar and co-workers.

It is clear from these results that previous ab initio calculations have been done at too low a level of theory to be conclusive. At the same time, the present results are certainly still not converged either with respect to basis set or description of electron correlation. The potential energy surface reported here is very flat along the critical interallylic distance coordinate connecting C_{2h} structures. The total energy varies by only 3 kcal/mol over the range of R from 1.64 to 2.19 Å while the wave function changes from biradicaloid to benzenoid. Because of the large change in the nature of the wave function, relative energies along this path are uncertain by more than 3 kcal/mol.

One could instead attempt to decide between paths based on the entropy of activation[3] which is −13 ± 1 cal/(mol·K⁻¹) for the chair path and −3 ± 4 cal/(mol·K⁻¹) for the boat path. At first sight the entropies in Table III seem to indicate the Dewar path is in good agreement with experiment. If the 1,5-hexadiene entropy is corrected for internal rotation around three single bonds a value closer to 107 cal/(mol·K⁻¹) is indicated.[16] With this value the aromatic synchronous paths seem more likely while the Dewar path would have an activation entropy nearer 20 cal/(mol·K⁻¹).

Supplementary Material Available: Listings of final coordinates for stationary points (3 pages). Ordering information is given on any current masthead page.

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