Rearrangements of Allene Oxide, Oxyallyl, and Cyclopropanone

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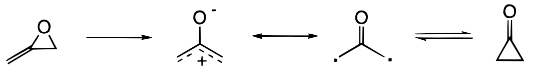
Received June 22, 1998. Revised Manuscript Received October 6, 1998

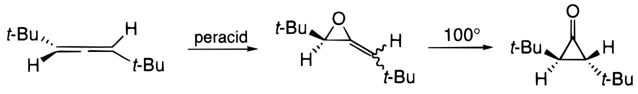
Abstract: A detailed theoretical study of the rearrangement of allene oxide to cyclopropanone and the racemization of substituted cyclopropanones and the isomerization of substituted cyclopropanones is presented. The rearrangement of allene oxide to cyclopropanone was found to proceed in a stepwise fashion in which allene oxide first undergoes conversion to oxyallyl via a newly found transition structure with subsequent ring closure of the oxyallyl to cyclopropanone. It is shown that a previously found transition structure is on the pathway that results in the racemization of chiral-substituted cyclopropanones. A new transition structure was also located that accounts for the previously observed conversion of *cis*-2,3-di-*tert*-butylcyclopropanone to its trans diastereomer. The discussion is based on the results of DFT and CASSCF methods. IRC calculations were carried out for all transition structures located. Single-point energies were calculated with the CASPT2N, QCISD(T), and UQCISD(T) methods. Good agreement was found between the calculated results and those available from experiment.

Introduction

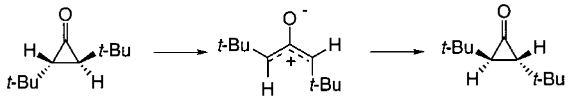
Oxyallyl (**1**) has long been considered as a potential intermediate or transition structure in the rearrangement of allene oxide (**2**) to cyclopropanone (**3**)[1−7] and in the ring opening and closing reactions of substituted cyclopropanones that result in racemization and isomerization.[8−15] Early experimental evidence for the existence of allene oxide as a viable species was based on the characterization of its reaction products,[1] since its apparent high reactivity precluded its isolation. However, in 1968 Camp and Greene reported that the epoxidation of 1,3-di-*tert*-butylallene gave the first isolable allene oxide, 1,3-di-*tert*-butylallene oxide,[3] which when heated to 100 °C underwent rearrangement to *trans*-2,3-di-*tert*-butylcyclopropanone. This report not only confirmed the existence of allene oxides, but also showed that they undergo facile rearrangement to cyclopropanones presumably through oxyallyls.

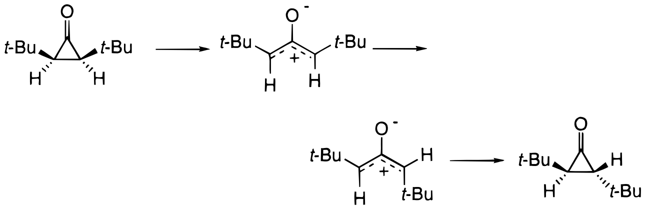


2 **1a** **1b** **3**



In 1970 Greene and co-workers subsequently demonstrated that enantiomerically enriched *trans*-2,3-di-*tert*-butylcyclopropanone undergoes racemization on heating and proposed that this reaction occurs via an oxyallyl intermediate.[10] More recently, Sorensen and Sun reported[15] the isolation of *cis*-2,3-di-*tert*-butylcyclopropanone and its subsequent isomerization to *trans*-2,3-di-*tert*-butylcyclopropanone. This result confirms that oxyallyl must be an intermediate. While the concerted disrotatory ring opening and closing can account for the racemization of *trans*-2,3-di- *tert*-butylcyclopropanone, it cannot be responsible for the isomerization of the cis diastereomer. Oxyallyl must be first formed as an intermediate and then undergo subsequent rearrangement before closing to the cyclopropanone.





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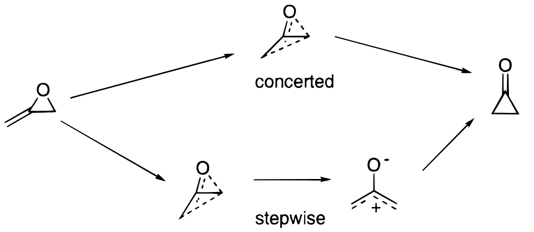
Scheme 1



Most theoretical studies have focused on the role of oxyallyl in the ring opening and closing reaction of cyclopropanone which leads to racemization of substituted cyclopropanones. The mechanistic details of the isomerizations of allene oxide and substituted cyclopropanones have received little attention. A theoretical study performed in 1994[12a] based on the finding that the calculated frequencies (CASSCF(4/4)/6-31G*) of **1** are all real showed the singlet state ($^1A_1$)[16] of **1** is an intermediate. The oxyallyl intermediate was computed to be about 28 kcal/mol higher in energy than cyclopropanone. A transition structure with C_s symmetry was also located on the potential surface, which presumably links oxyallyl with cyclopropanone.

There still remain several unanswered questions concerning the mechanism of these rearrangements. (1) Does allene oxide (**2**) rearrange directly to cyclopropanone (**3**) in a concerted reaction (see Scheme 1)? (2) If not, is oxyallyl an intermediate in the rearrangement? (3) What is the transition structure for the isomerization of oxyallyl responsible for the observed isomerization[15] of *cis*-2,3-di-*tert*-butylcyclopropanone? The results of the following analysis based on an ab initio study provide answers to these questions.

Computational Methods

Calculations were performed with the GAUSSIAN 94 (the majority of the geometry optimizations),[17] GAMESS 97[18] (CASSCF(4,4) optimizations of **1**, **2**, and **4**), and MOLCAS-4 computational packages.[19] All structures were optimized with the density functional method (DFT) (Becke's three-parameter functional, B3LYP or UB3LYP, was employed[20]) as well as with CASSCF(4,4).[21] Two basis sets were used with the DFT calculations (6-31G* and 6-311G**)[22] and one (6-31G*) for the CASSCF calculations.[23] Due to the instability of the restricted solutions for structures **1**, **4**, **6**, and **10** the unrestricted forms of the single determinant based methods have been used throughout for these systems. Harmonic frequencies obtained with both methods were used to characterize all stationary points (minima or transition structures) and to compute zero-point energies.[24] Intrinsic reaction coordinate (IRC) calculations[25] ((U)B3LYP/6-31G* and CASSCF(4,4)/6-31G*) were carried out for each transition structure located to determine which two minima were linked by the transition structure.

Table 1. Q1-Diagnostic Values[a]

compd	QCISD(T)//(U)B3LYP	UQCISD(T)//(U)B3LYP
1	0.0303	0.0231
2	0.0149	
3	0.0152	
4	0.0315	0.0325
6	0.0849	0.0592
10	0.2342	0.2284

[a] 6-31G* basis set used.

Single-point CASPT2N calculations[26] using a CASSCF(10,11) reference function were also performed at (U)B3LYP/6-31G* geometries. On the basis of the results of several test calculations, the active space of 10 electrons and eleven orbitals was chosen, and it includes all natural orbitals with occupation numbers between 0.02 and 1.98 for each structure considered. Additional orbitals were included to ensure smooth convergence. The molecular orbitals of the CASSCF wave function were fully optimized.[27] Single-point energy calculations[24] at the (U)B3LYP/6-31G* geometries obtained with the QCISD(T) and UQCISD(T) methods were also performed.[28] Lee and co-workers[29] proposed a criterion to estimate the importance of nondynamical correlation effects and to verify the reliability of singe-determinant approaches for the description of molecular and electronic structure. On the basis of the weighted Euclidean norm of the converged amplitudes of the single excitation operator, the Q1- (T1-) diagnostic in the QCISD (CCSD) method above 0.02, indicates large nondynamical correlation effects, and a change to multireference approaches might improve the results significantly. In Table 1 the values of this Q1-diagnostic are presented and the single-point energies are given in Table 2. According to these results structures **1**, **4**, **6**, and **10** should preferably be described by using multireference approaches such as CASPT2N/CASSCF.

Results and Discussion

Racemization of Chiral Cyclopropanones. Camp and Greene suggested that the formation of an oxyallyl intermediate could account for the racemization of *trans*-2,3-di-*tert*-butylcyclopropanone.[10] On the other hand, a concerted reaction in which oxyallyl is a transition structure rather than an intermediate could also account for their observation. However, recent studies on *cis*-2,3-di-*tert*-butylcyclopropanone provide strong experimental evidence that oxyallyl is an intermediate rather than a transition structure.[15] In addition the results of CASSCF(4,4)/6-31G* calculations on oxyallyl showed that indeed oxyallyl is an intermediate with C_{2v} symmetry.[12a] A transition

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(16) It was found in ref 12a that the triplet state ($^3B_2$) of **1** is its ground state, being slightly more stable than its singlet state ($^1A_1$).

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(22) Originally only the 6-31G* basis set was employed with the DFT calculations, but on the suggestion of a referee we repeated all DFT optimizations and frequency calculations with the 6-311G** basis set. Only very minor changes in relative energies and structures were found on going to this larger basis set. Therefore the discussion is limited to the DFT calculations done with the 6-31G* basis set. The results obtained with the larger basis set may be found in Tables 2 and S1.

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(24) Total energies and zero-point energies are given in Table S1 (Supporting Information).

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(27) The orbital specifications of the CASSCF reference functions are given in Tables S2−S4 (Supporting Information).

(28) Pople, J. A.; Head-Gordon, M.; Raghavachari, K. *J. Chem. Phys.* **1987**, *87*, 5968.

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Table 2. Relative Energies[a] (in kcal/mol) of **1**−**4**, **6**, and **10**

method[b]	3	2	1	4	6	10
MP2//SCF/4-31G[c]	0	4.4	45.2			48.7
CASSCF(4,4)//CASSCF(4,4)	0[d]	18.9	24.0[d]	24.3[d]	41.2	28.7
CASPT2N/CASSCF(10,11)//(U)B3LYP	0	12.6	30.6	28.6	41.8	38.9
(U)B3LYP//(U)B3LYP	0	11.3	27.4	29.6	41.2	36.2
(U)B3LYP//(U)B3LYP[e]	0	12.0	27.3	28.8	40.4	36.0
QCISD(T)//B3LYP	0	12.5	33.4	29.8	43.9	87.9
UQCISD(T)//UB3LYP	0	12.5	31.4	33.6	50.4	37.3

[a] ΔE°; zero-point energies were computed with unscaled frequencies (CASSCF(4,4)/6-31G* frequencies for CASSCF(4,4) calculations and (U)B3LYP/6-31G* for DFT calculations, QCISD(T), UQCISD(T), and CASPT2N single-point energies). [b] Unless otherwise noted the 6-31G* basis set was used. [c] ΔE°, ref 34. [d] Reference 12a. [e] 6-311G** basis set.

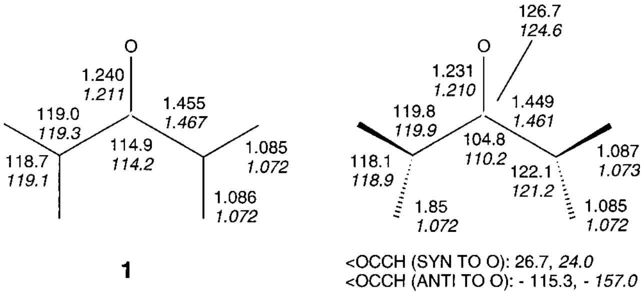

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Figure 1. DFT and CASSCF[12a] (in italics) geometries of **1** and **4**. Bond lengths in angstroms and angles in degrees.

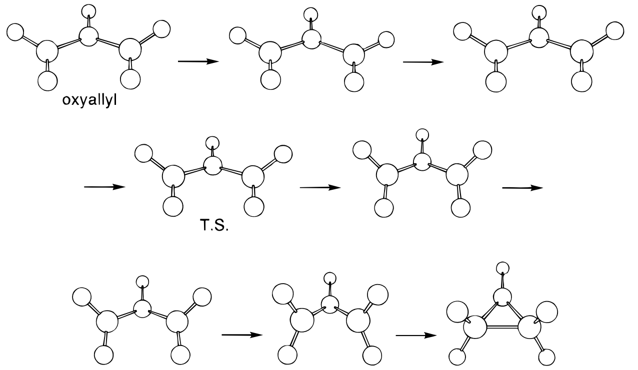
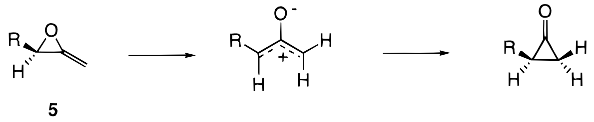


Figure 2. The UB3LYP/6-31G* IRC pathway of the racemization of cyclopropanone.

structure with C_s symmetry was also located on the potential surface which presumably links oxyallyl with the two cyclopropanones in a degenerate reaction, though no IRC calculations were performed to confirm this.

The UB3LYP method with the 6-31G* basis set was used to locate the oxyallyl intermediate as well as a "disrotatory" transition structure (**4**)[30] which were found to be similar to those found earlier with the CAS method (see Figure 1).[12a] Energies relative to the energy of cyclopropanone are given in Table 2. The results of the DFT IRC reveal (see Figure 2) that the transition structure (**4**) links cyclopropanone to oxyallyl in the degenerate rearrangement of cyclopropanone that had been earlier proposed to account for the racemization of chiral *trans*-disubstituted cyclopropanones. It is interesting to note that the DFT method gives an activation energy (ΔE°) of 29.6 kcal/mol that is in very close agreement with the experimental free energy of activation (29.1 kcal/mol) for the racemization of (+)-*trans*-2,3-di-*tert*-butylcyclopropanone in isooctane.[10] Earlier CAS calculations gave a value of 21.9 kcal/mol for ΔE° of this reaction.[12a] However, the calculations based on CASPT2N/6-31G* and performed by these authors for cyclopropanone and oxyallyl gave a barrier of "about 28 kcal/mol". This is an approximate value, since it was based on the energy difference of cyclopropanone and oxyallyl rather than the transition structure **4**. Finally it is noted that for single-point CASPT2N calculations performed for geometries obtained with the DFT approach the transition structure **4** is found to be lower in energy than oxyallyl (**1**). This is most likely due to the sensitivity of the energy of **4** to the degree of rotation of the methylenes in the transition structure, and this discrepancy might therefore be accounted for by the geometry of the CASPT2N transition structure having a smaller degree of rotation (earlier transition structure) than that found with the DFT method.

Rearrangement of Allene Oxide to Cyclopropanone. Due to the instability of allene oxide experimental evidence for the rearrangement of allene oxides to cyclopropanones has been limited to substituted allene oxides or to indirect evidence based on the analysis of reaction products of allene oxides prepared in solution. Simple alkyl derivatives of allene oxide are known to undergo polymerization[3,5] or attack by nucleophiles[5] before the rearrangement can occur. As mentioned in the Introduction, Camp and Greene isolated the first stable derivative of allene oxide, 1,3-di-*tert*-butylallene oxide, and found that it rearranged to *trans*-2,3-di-*tert*-butylcyclopropanone.[3] Experimental evidence for the possible intermediacy of oxyallyls in the rearrangement of allene oxides to cyclopropanones was reported by Chan and Ong.[5] They found that simple monosubstituted allene oxides (**5**, R = alkyl) under the conditions in which they were prepared were attacked by nucleophiles before rearrangement to cyclopropanones could occur. On the other hand, **5** (R = phenyl) underwent the rearrangement to 2-phenylcyclopropanone under the same conditions. Chan and Ong argued that the phenyl group stabilizes the positive charge in the oxyallyl intermediate enhancing its rate of formation from the allene oxide over that of attack of the nucleophile. However the phenyl group might also stabilize the transition structure (see Scheme 1) in a concerted rearrangement.



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R = alkyl, phenyl

Early calculations were limited to the computation of the relative energies of allene oxide, oxyallyl, and cyclopropanone. With the exception of extended Hückel calculations,[31] in all cases cyclopropanone was found to be more stable than allene oxide with oxyallyl significantly higher in energy than either **2** or **3**.[7−9,12a,32−34] In Table 2 the relative energies of **1**−**3**, including the results of the best calculations performed to date, are summarized.

While the experimental evidence has been interpreted as supporting oxyallyl as an intermediate in the rearrangement of allene oxide to cyclopropanone, it does not rule out a concerted pathway between **2** and **3**. To determine the exact nature of

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(30) On the suggestion of a referee an extensive search for the forbidden "conrotatory" transition structure was carried out without success. Consequently it appears likely that the forbidden transition structure does not exist. We found a similar situation in the past when an exhaustive search for the forbidden suprafacial transition structure for the 1,5-hydrogen shift in the rearrangement of pentadiene failed (Hess, B. A., Jr.; Schaad, L. J.; Pancir, J. *J. Am. Chem. Soc.* **1985**, *107*, 149).

(31) Hoffmann, R. *J. Am. Chem. Soc.* **1968**, *90*, 1475.

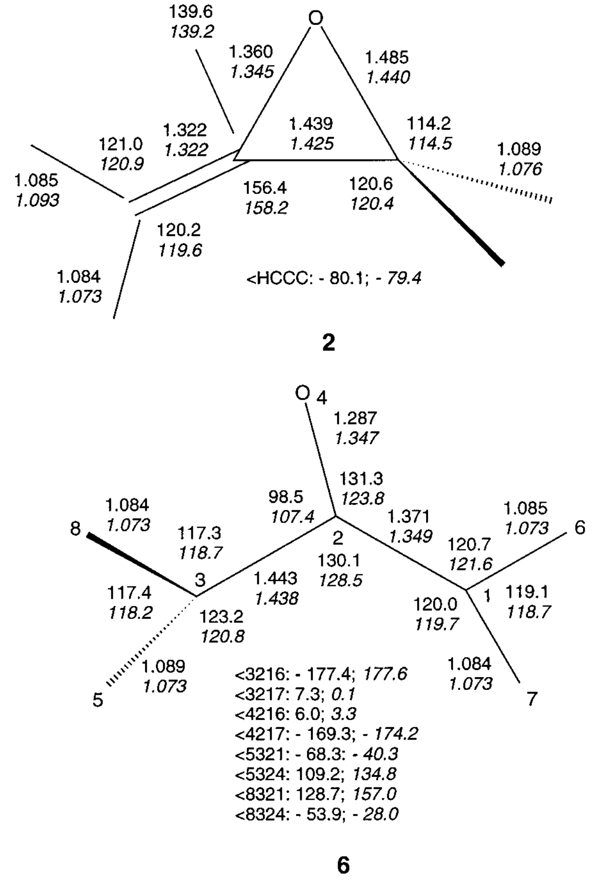

Figure 3. Optimized (U)B3LYP/6-31G* and CASSCF(4,4)/6-31G* (in italics) structures of allene oxide and transition structure **6** linking allene oxide with oxyallyl.

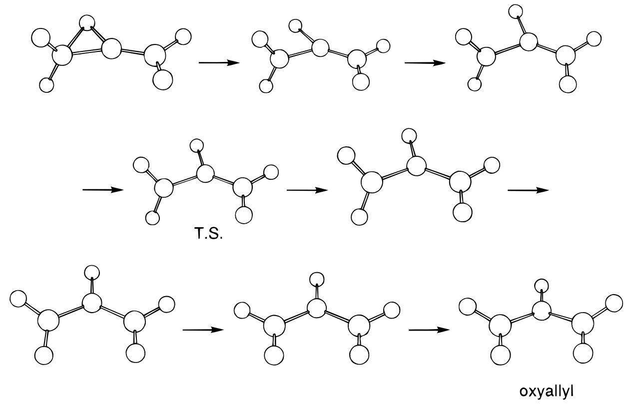

Figure 4. The UB3LYP/6-31G* IRC pathway leading from allene oxide to oxyallyl.

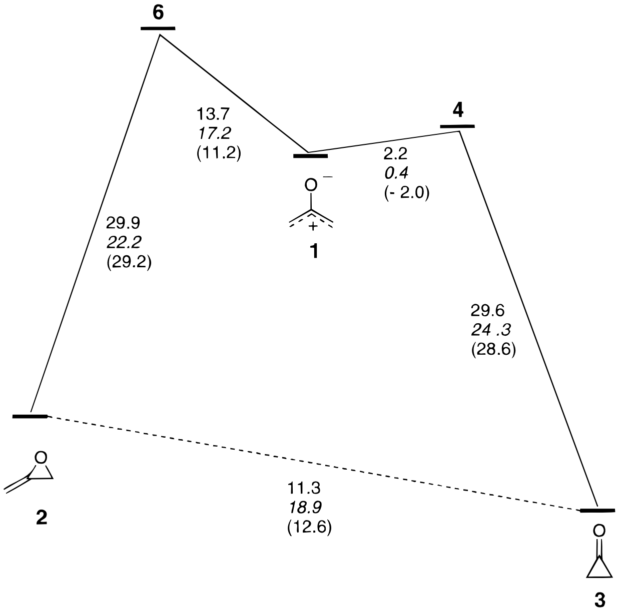

Figure 5. The overall energy profile for the conversion of allene oxide to cyclopropanone. Energies (Δ*E*°) in kcal/mol from (U)B3LYP, CAS-(4,4)/6-31G* (in italics), and CASPT2N (in parentheses) calculations.

this rearrangement a search for the transition structure on the pathway of this rearrangement was undertaken. A transition structure was located (**6**) with an energy higher than allene oxide (Δ*E*° (kcal/mol): DFT, 29.9; CAS, 22.2; and CASPT2N, 29.2, see Table 2), and it appears to be on the pathway of the ring opening of the epoxide ring in **2**. Optimized structures (CAS and DFT) of allene oxide (**2**) were also obtained and are presented along with those of **6** in Figure 3. Inspection of **6** reveals that the epoxide has undergone significant ring opening (∠C−C−O = 98.5° (DFT), 107.4° (CAS)). One also sees that the plane of the vinyl methylene group has begun to rotate out of the plane of the original epoxide ring while the plane of the epoxide methylene group is rotating toward the plane of the original epoxide ring. These motions are in fact "conrotatory" in nature. While it appears that **6** is the transition structure for the ring opening of the epoxide ring in allene oxide, it is not possible to conclude to what structure **6** is leading (e.g., oxyallyl or cyclopropanone). However, IRC calculations performed for **6** with the structures obtained with both DFT and CAS methods show that **6** in fact links allene oxide with oxyallyl (see Figure 4). Hence the ring opening of the epoxide in allene oxide does not lead directly in a concerted pathway to cyclopropanone but rather at first to oxyallyl. Selected points along the reaction path are depicted in Figure 4 for the UB3LYP/6-31G* IRC. It is seen in Figure 4 that proceeding from **6** the C−C−O angle continues to increase to the point where it bisects the C−C−C angle while the two methylene groups continue to rotate in a disrotatory fashion until the overall structure is close to having C_s symmetry. At this point the rotation of the original vinyl methylene group "changes direction" and the two methylene groups rotate in a conrotatory fashion toward the oxyallyl intermediate. The results of the CAS IRC are very similar to those of the DFT method with the exception that the original vinyl methylene group changes its direction of rotation prior to the transition structure. Beginning from allene oxide the two methylene groups rotate in a disrotatory fashion; but their rotations become conrotatory prior to the transition structure, whereas in the DFT IRC this change occurs on the pathway after the transition structure is formed.

The picture is now complete for the rearrangement of allene oxide to cyclopropanone. First allene oxide rearranges through transition structure **6** to oxyallyl, which then closes in a disrotatory fashion through transition structure **4.** The overall reaction is depicted in Figure 5. One of the most striking aspects of these results is the close agreement of the energies calculated with the DFT and CASPT2N methods. Therefore one may conclude that the DFT method gives more reliable results than CASSCF(4,4). This conclusion is also apparent from Table 2 where the relative energies of six species on the C_3H_4O potential surface are compared to those of cyclopropanone.

Given the stepwise mechanism for the rearrangement of allene oxide to cyclopropanone, the stereochemistry of the overall rearrangement may be summarized as in Scheme 2. The ring opening of **7** can proceed to form the isomeric oxyallyls **8a**

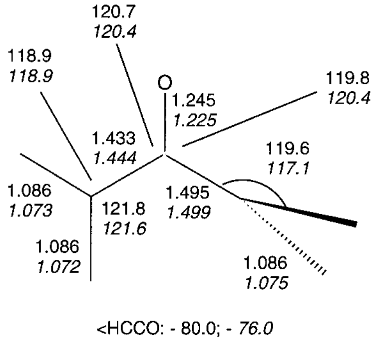

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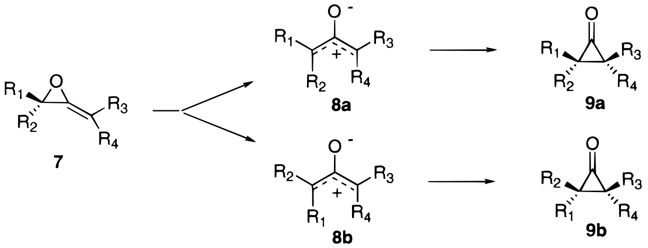
Figure 6. UB3LYP/6-31G* and CASSCF(4,4)/6-31G* (in italics) geometry of **10**. Bond lengths in angstroms and angles in degrees.

Scheme 2



and **8b**. If R$_1$ is significantly bulkier than R$_2$, **8a** will be formed to a greater extent than **8b**. It is this step that will determine the ratio of the two diastereomers (**9a** and **9b**) in the final product mixture. If **7** is chiral, because of the intermediacy of the planar oxyallyls (**8**), only racemic mixtures of **9a** and **9b** will be formed. Finally if R$_4$ is significantly bulkier than R$_3$, there is the potential for **9a** and **9b** to undergo rearrangement (see next section) to the more stable oxyallyls (with R$_4$ syn to the oxygen).

Isomerization of Substituted Cyclopropanones. Unlike in the case of the racemization of chiral cyclopropanones where only mirror images of a single transition structure connect cyclopropanone and oxyallyl, the isomerization of cyclopropanones requires a second transition structure. In the racemization the oxyallyl once formed needs only to continue along the disrotatory pathway to reach the mirror image of the starting material. However, for a cyclopropanone to isomerize, oxyallyl itself must undergo a rearrangement that must involve an additional transition structure. A likely candidate for this role is a "perpendicular" oxyallyl[34] in which one of the methylene groups is rotated perpendicular to the plane of the other atoms. This structure of oxyallyl along with "planar" oxyallyl was previously considered by Ortiz.[34] He found using single-point MP2/6-31G* calculations done at partially optimized 4-31G geometries that the planar form is more stable than the perpendicular one by only 3.5 kcal/mol. A search for a perpendicular form of oxyallyl yielded the transition structure **10** (see Figure 6), which is higher in energy (see Table 2) than oxyallyl ($\Delta E°$ (kcal/mol): DFT, 8.8; CAS, 4.3; CASPT2N, 8.3).[35] An IRC calculation confirmed that **10** is the transition structure which links the oxyallyls in a concerted, degenerate rearrangement. The nature of the overall isomerization process (see Figure 7) is such that cyclopropanone must first open to the oxyallyl ($\Delta E°$ (kcal/mol): DFT, 29.6; CAS, 24.3; CASPT2N, 28.6) with a second barrier to be overcome before isomerization can occur. This raises the interesting possibility that chiral disubstituted cyclopropanones might racemize without undergoing formation of the diastereomers. In fact the racemization of *trans*-1,2-di-*tert*-butylcyclopropanone[10] discussed above is such an example, but here the bulky *tert*-butyl groups presumably prevent isomerization to the cis diastereomer. Sorensen and Sun have calculated (B3LYP/6-31G**) the *cis* diastereomer to be 9 kcal/mol higher in energy than the trans.[15] Interestingly they also estimate the energy difference between di-*tert*-butyl oxyallyl (both *tert*-butyl groups syn to the oxygen) and the corresponding perpendicular oxyallyl transition structure to be 16 kcal/mol. This barrier to isomerization of the oxyallyls is significantly higher than the presently computed value for the unsubstituted oxyallyl ($\Delta E°$ (kcal/mol): DFT, 8.8; CAS, 4.3; CASPT2N, 8.3). However, the presence of the *tert*-butyl groups might significantly alter this energy difference from that of the unsubstituted case. In addition, the calculated numbers are for the gas phase, and this difference might also be in part due to solvent effects. However, there is both computational[12] and experimental evidence[10] that the rate of the ring opening of cyclopropanone to oxyallyl is only mildly affected by solvent.

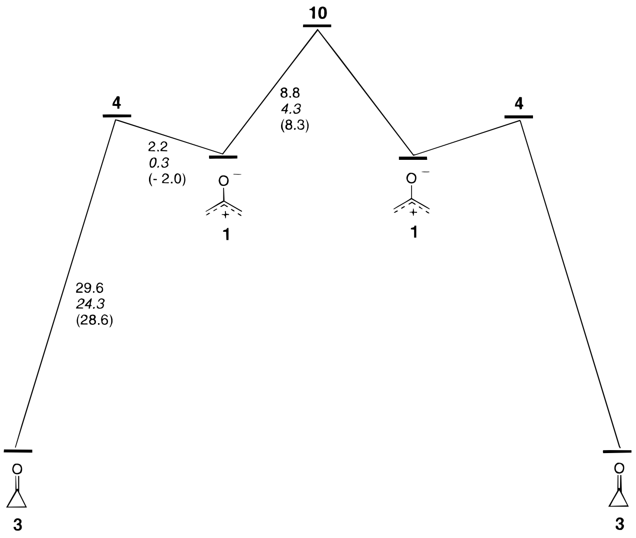


Figure 7. The overall energy profile for the isomerization of cyclopropanone. Energies ($\Delta E°$) in kcal/mol from (U)B3LYP, CAS-(4,4)/6-31G* (in italics), and CASPT2N (in parentheses) calculations.

As mentioned above, the experimental results of Sorensen and Sun provide strong support for the existence of oxyallyl as an intermediate that is capable of undergoing an isomerization presumably through a transition structure similar to that of **10**. The DFT and CAS calculations reported here describe qualitatively exactly the pathway described by Sun and Sorensen in 1997 based on their experimental findings.[15]

Conclusions

On the basis of DFT and CASSCF calculations, it has been shown that allene oxide rearranges to cyclopropanone through the intermediate oxyallyl. Oxyallyl was also found to be an intermediate common to both the racemization and isomerization reactions of substituted cyclopropanones. Although allene oxide is higher in energy than cyclopropanone by ~12 kcal/mol, and therefore closer in energy to the common intermediate oxyallyl for their respective ring opening reactions, the energy required

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[35] As seen in Table 2 the QCISD(T) energy of **10** is obviously incorrect. This is perhaps not surprising given its very high Q1 value (0.2342).

for the ring opening of both **2** and **3** to give **1** is about the same (∼29 kcal/mol, see Figure 5). A "perpendicular" oxyallyl transition structure was located linking two oxyallyls, which accounts for the isomerization reactions of substituted cyclopropanones. The pathways for these reactions are in complete accord with experimental findings.

It is interesting to note that the DFT results are in good accord with those obtained with the CASPT2N/CAS(10,11) method. What is also surprising is that even for structures **1**, **4**, **6**, and **10** with a Q1 greater than 0.02[29] the DFT results are in good accord with those of CASPT2N/CASSCF. This adds strength to the growing evidence[18,36−42] that the DFT method is extremely useful for studying reaction pathways even when they involve diradical intermediates or species with potential diradical character. Finally we note the unexpected result that the QCISD(T) method with the exception of **10** gives relative energies (Table 2) very close to those of CASPT2N/CASSCF and in better agreement than the UQCISD(T) energies.

Acknowledgment. This research was partially supported by NATO (Grant No. 920007). One of the authors (U.E.) wishes to thank the Deutsche Forschungsgemeinschaft (Graduiertenkolleg Struktur-Eigenschafts-Beziehungen bei Heterocyclen) for financial support.

Supporting Information Available: Total and zero-point energies of **1**−**4**, **6,** and **10** (Table S1), orbital specifications of the CASSSCF(4,4) and CASSCF(10,11) reference functions (Tables S2 and S3), and occupation numbers of the active space natural orbitals obtained with CASSCF(10,11) (Table S4) (4 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

JA9821652

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