The Origin of Regioselectivity in α-Cleavage Reactions of Cyclopropenethiones: Potential Role of Pseudo-Jahn–Teller Effect in Substituted Cyclopropenyl Systems

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Received December 10, 1985

Arylalkylcyclopropenethiones undergo highly regioselective photochemical α-cleavage via thioketene carbene intermediates, giving rise to products derived from the less stabilized carbene. UHF MINDO/3 calculations provide an insight into this unexpected regioselectivity. The $n\pi^*$ triplet of cyclopropenethione is calculated to have a highly unsymmetrical geometry with an elongated C–C bond, a delocalized thiaallyl fragment, and a pyramidal radicaloid carbon (which eventually becomes the carbene center). From this molecular electronic structure, aryl group stabilization is expected to be more effective at the thiaallyl group rather than at the pyramidal radical center. Thus, the stability of the substituted triplet thione rather than that of the thioketene carbene determines the preferred regiochemistry of cleavage. The unusual structure of the cyclopropenethione triplet is suggested to be related to one of the Jahn–Teller distorted forms of the cyclopropenyl radical. An alternative symmetrical structure is adopted by the corresponding triplet of cyclopropenone, partly accounting for its differing photobehavior. A similar structural dichotomy is demonstrated for the corresponding radical anions as well.

One of the more recently discovered photoreactions of thiocarbonyls is the α-cleavage process occurring in the $n\pi^*$ triplet state.[1] For this Norrish-type I reaction involving diphenylcyclopropenethione, a 1,3-diradical and thioketene carbene were postulated to be the primary intermediates.[2] Investigation of the reaction in the case of arylalkylcyclopropenethione revealed a remarkable regioselectivity as illustrated in Scheme I, with the products originating from the less stable carbene.[3] One explanation for this unexpected regioselectivity is based on the dynamics of the photoprocess.[4] The efficiency of radiationless decay from the triplet cyclopropenethione to the thioketene carbene is expected to be inversely dependent on the energy gap between the two surfaces. Closer approach is envisaged for the less stable alkyl-substituted diradical/carbene than for the corresponding phenyl-substituted ones. Thus the less stable cleavage products result from a more efficient funneling process. While the dynamics of the photoprocess can undoubtedly play a crucial role, it is conceivable that the product selectivity is determined at an early stage itself through the structural and energetic predilections of the reactant in the excited hypersurface. We now show by means of semiempirical molecular orbital calculations that such a possibility may indeed be responsible for the unconventional regioselectivity in the case of cyclopropenethiones. We have also obtained the preferred geometries and energies of several stationary points on the triplet cyclopropenone potential energy surface. These results provide an understanding of the differing photobehavior of cyclopropenones and the corresponding thiones. Several of these triplet structures are demonstrated to be novel examples of alternative Jahn–Teller distorted forms derived from the cyclopropenyl moiety.

Computational Details

All calculations were performed with the MINDO/3 method.[5] Open shells (triplets and doublets) were treated by the unrestricted Hartree–Fock method (UHF).[6] Full geometry optimization without assuming any symmetry was carried out for each system. In addition, selected symmetry constraints were imposed to obtain the energies of less stable conformers. Stationary points were characterized by diagonalizing the force constant (Hessian) matrix. Hessian indices (number of negative eigenvalues) of 0 and 1 correspond to minima and transition states,[7] respectively.

Results

The calculated structures, heats of formation, and Hessian indices for low-lying $n\pi^*$ triplet of cyclopropenethione and cyclopropenone are shown in Figures 1 and 2, respectively. The corresponding data for the ground-state singlet are also included for reference. The most remarkable result is the highly unsymmetrical geometry obtained for the minimum of $n\pi^*$ triplet cyclopropenethione. The corresponding ketone prefers a symmetrical structure (C_2 symmetry), suggesting a fundamental difference in the electronic structures of these triplets.

In order to unravel the electronic origins of the structural preferences, the radical anion of cyclopropenethione and the corresponding ketone were also examined. These results, presented in Figure 3, selectively highlight the role of π interactions in inducing structural deformations. Mono- and dimethylcyclopropenone and mono- and dimethylcyclopropenethione were also examined to probe the substituent effect. The calculated geometries and heats of formation of the ground state and the most stable triplet of these systems are given in Figure 4.

In all the structure drawings, special attention is drawn to the out of plane bending angles of various atoms. The angle $\phi(X)$ corresponds to the angle between CX bonds and the ring plane.

Discussion

The geometries and energies of the parent cyclopropenethione and cyclopropenone in the ground and excited states are considered first. In the next section, differences in the two systems are interpreted in terms of

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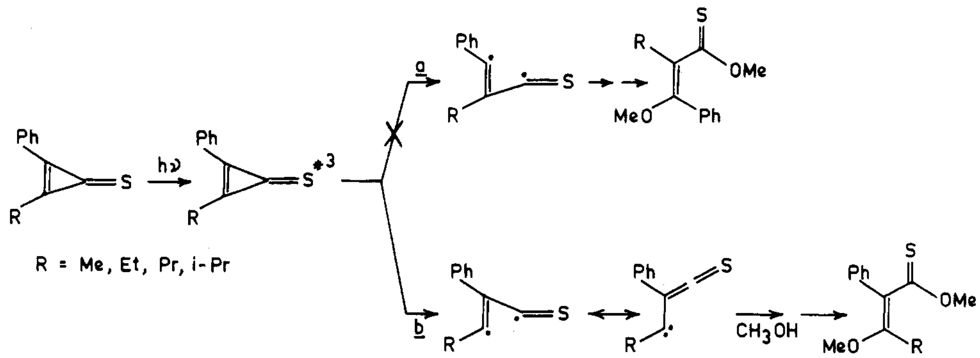
[7] Murrell, J. N.; Laidler, K. J. *Trans. Faraday Soc.* **1968**, *64*, 371.

0022-3263/86/1951-3630$01.50/0

Scheme I



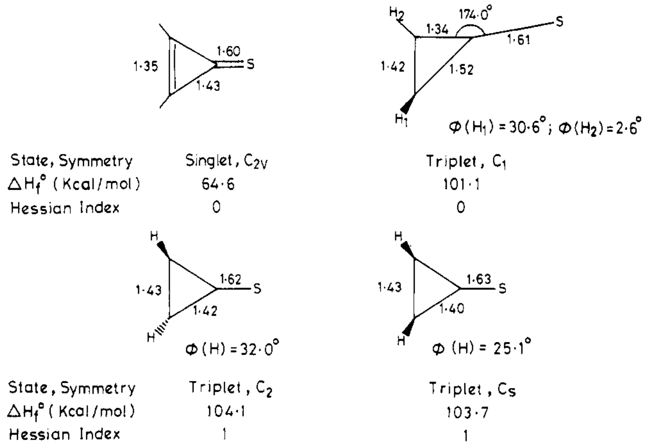


Figure 1. MINDO/3 results for singlet and nπ* triplet cyclopropenethione. The top right structure corresponds to the minimum energy form for the triplet. The two lower structures were obtained by imposing symmetry constraints during geometry optimization.

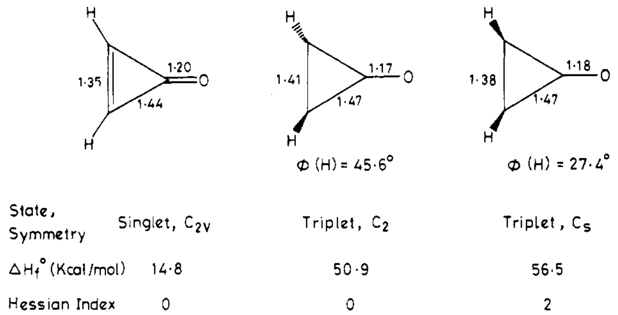


Figure 2. MINDO/3 results for singlet and nπ* triplet cyclopropenone. The middle structure corresponds to the minimum energy form for the triplet. The right most structure was obtained by imposing C_s symmetry constraints during geometry optimization.

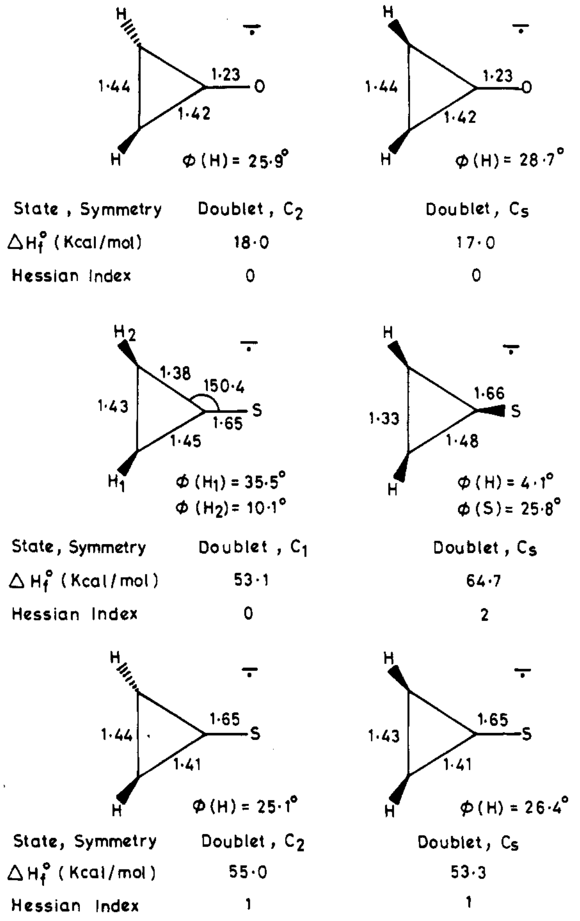


Figure 3. MINDO/3 results for radical anions of cyclopropenone and cyclopropenethione. The top two structures are both true minima obtained from different initial geometries of cyclopropenone radical anion. The middle left structure is the true minimum for cyclopropenethione radical anion. The three remaining structures were obtained by imposing symmetry constraints during geometry optimization.

orbital interactions present in a cyclopropenyl radical fragment containing a 2π electron donor substituent. Calculations on related model systems are used to highlight σ and π contributions in determining the preferred geometry. Finally, substituent effects on the relative stabilities of isomeric triplet geometries are discussed and these are utilized to understand the observed regiochemistry in the α-cleavage reaction of cyclopropenethiones.

Structures of Cyclopropenethione and Ketone. The singlet ground-state geometries of cyclopropenethione and cyclopropenone are, as expected, quite similar, both having C_{2v} symmetry with nearly the same ring CC bond lengths (Figures 1 and 2). The minimum energy geometries of the nπ* triplet state are, however, dramatically different. The thione excited-state geometry is highly unsymmetrical with three unequal CC bonds and a nearly linear CCS fragment. Interestingly, only one of the hydrogen atoms is significantly bent out of the heavy atom plane. It is easily recognized that the structure tends toward the geometry of the α-cleavage intermediate, viz., thioketene carbene, with the longest CC bond in the ring corresponding to the bond being broken and the pyramidal carbon becoming the ultimate carbene center.

Two other higher energy structures with C_2 and C_s symmetry were obtained by imposing constraints during geometry optimization. While these are only slightly less stable than the C_1 form, analysis of Hessian indices and the corresponding transition vectors indicate that both symmetrical structures are indeed transition states for the

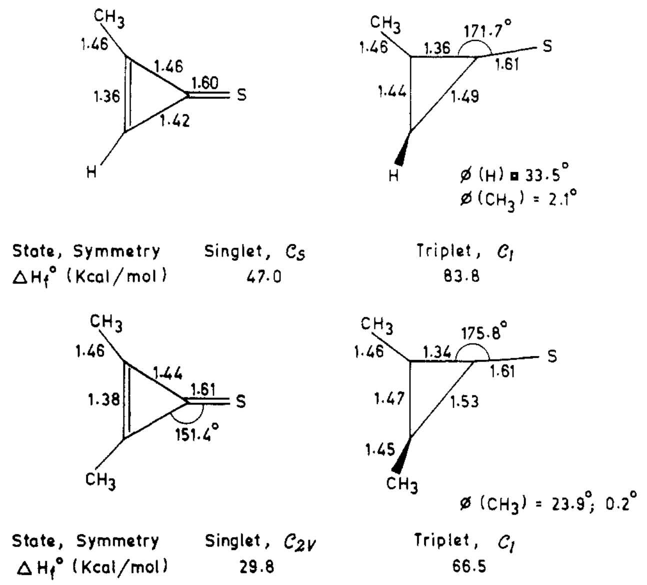
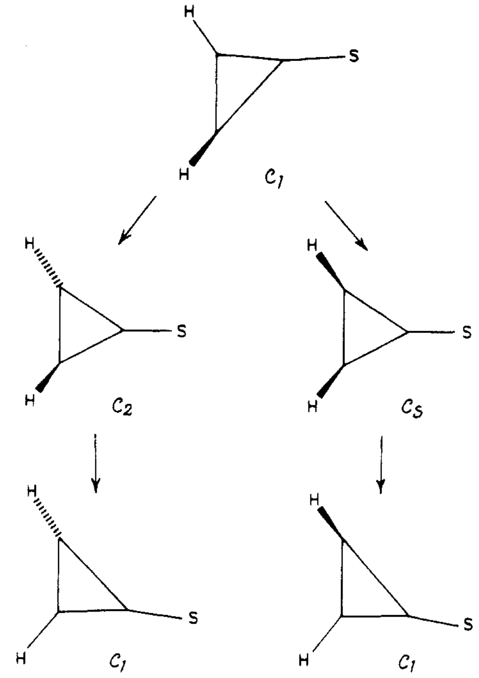


Figure 4. MINDO/3 results for singlet and nπ^* triplet monomethylcyclopropenethione and dimethylcyclopropenethione.

Scheme II



interconversion of two equivalent C_1 forms (Scheme II).

In striking contrast to the structural preference of the thione, the cyclopropenone triplet is calculated to have a C_2 minimum. All attempts to obtain an unsymmetrical structure analogous to the thione triplet led to the C_2 form on geometry optimization. A C_s structure with cis hydrogen atoms was found to be 6 kcal/mol higher in energy with a Hessian index of 2.

The calculated structures clearly point to a difference in the detailed electronic structure in the excited-state cyclopropenethione and ketone. The computed energetics reinforce the differences between the two systems. Decarbonylation from the triplet ketone is calculated to be highly exothermic (ca. 48 kcal/mol) while the loss of CS from triplet thione is calculated to be slightly endothermic (ca. 6 kcal/mol). The absolute values of these reaction energies are probably in gross error principally due to the use of the UHF procedure for the triplets and also because of the inability of the approximate MO method to make a quantitative estimate of strain in the small ring system. However, the calculated difference is large enough to be in qualitative agreement with the observed reactivity pattern.[8]

The unsymmetrical nature of the nπ^* triplet of cyclopropenethione will ensure a well defined regioselectivity in the α-cleavage process in substituted derivatives, provided the pseudorotation indicated in Scheme II is not facile. The relative substituent stabilization at the two nonequivalent carbon atoms will then determine the product. In order to predict substituent effects, an understanding of the orbital pattern and charge distribution in the excited state is essential. These aspects are considered in the following section.

Orbital Interactions in the Excited State. In both cyclopropenone and cyclopropenethione, the system is considerably polarized in the ground state, with two electrons nearly localized in the unique heavy atom and the remaining two delocalized as an aromatic cyclopropenium ion. Excitation of an electron from the n_X orbital into a π^* orbital necessarily places an extra π electron in the ring. The nπ^* triplet can therefore be considered to be a cyclopropenium radical having a 2π electron donor substituent. Such an analysis suggests interesting structural consequences.

As is well-known,[9] the cyclopropenium radical with D_{3h} symmetry is electronically unstable, being subject to Jahn–Teller distortion. While numerous authoritative discussions[10] are available, the effect may be viewed in simple terms as follows. In the D_{3h} geometry, the odd electron can be placed in one of the doubly degenerate pair of orbitals shown in the middle of Figure 5. If the symmetric orbital ψ_{2s} is occupied, the system will be stabilized by a distortion that shortens one bond while lengthening the other two, leading to the enyl structure. A further distortion to the C_s form by pyramidalizing the unique carbon atom will localize the radical center and reduce antiaromatic destabilization.[11] The corresponding structure is the preferred one for the unsubstituted cyclopropenyl radical on the basis of the ab initio as well as MINDO/3 calculations.[12] Alternatively, placing the odd electron in the antisymmetric ψ_{2a} will lead to the allyl geometry with a unique long bond. Secondary trans and cis distortions of the hydrogen atoms out of the ring plane lead to further stabilized C_2 and C_s forms. For the parent system, these geometries are calculated to be slightly less stable than the C_s enyl structure. The former structure are not indicated to be true minima; they are transition states for the pseudorotation process interconverting three equivalent enyl forms.

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[12] (a) Hoffmann, M. R.; Laidig, W. D.; Kunn, K. S.; Fox, D. J.; Schaefer, H. F. *J. Chem. Phys.* **1984**, *80*, 338. (b) Poppinger, D.; Radom, L.; Vincent, M. A. *Chem. Phys.* **1977**, *23*, 437. (c) Baird, N. C. *J. Org. Chem.* **1975**, *40*, 624. (d) Shanshal, M. Z. *Z. Naturforsch., A: Astrophys., Phys., Phys. Chem.* **1971**, *26A*, 1336. (e) Pancir, J.; Zahradnik, R. *Tetrahedron* **1976**, *32*, 2257. (f) Winkelhofer, G.; Janoschek, R.; Fratev, F.; Spitznagel, G. W.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1985**, *107*, 332.

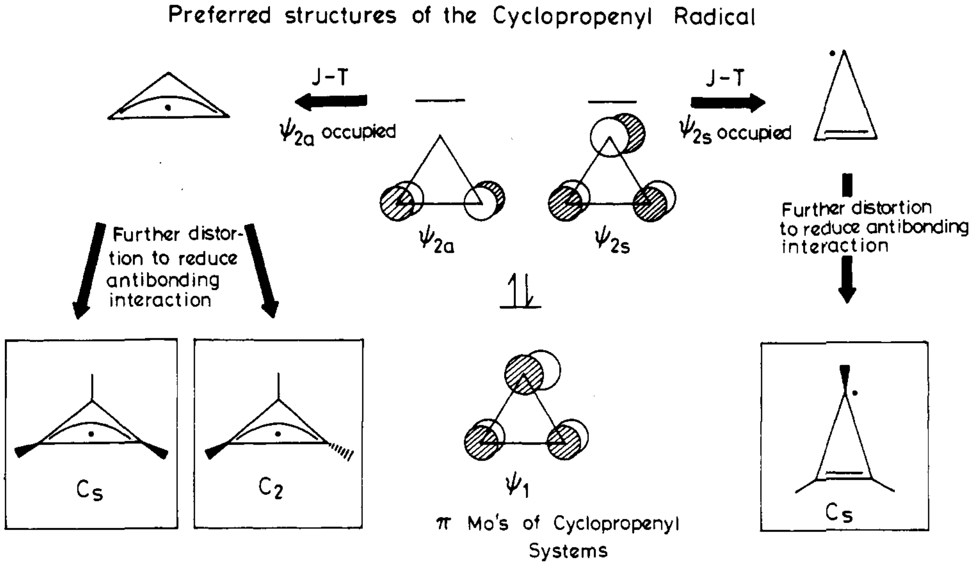

Figure 5. The π orbital pattern of the cyclopropenium radical and the resulting Jahn–Teller forms. The preferred stationary points are shown in boxes.

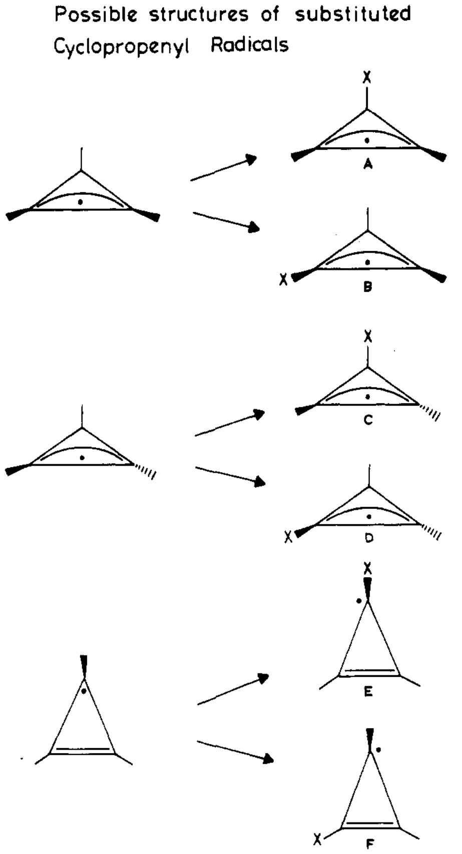

Figure 6. The six possible isomeric Jahn-Teller structures (A–F) of substituted cyclopropenyl radicals.

The various $n\pi^*$ triplet-state geometries as well as their relative energies calculated for cyclopropenethione and cyclopropenone (Figures 1 and 2) are strongly reminescent of the Jahn–Teller surface of the cyclopropenyl radical.[13] By placing a substituent at one of the two nonequivalent positions in each of the three possible structures of the $C_3H_3^{\bullet}$ system, six possible pseudo-Jahn–Teller forms may be derived (Figure 6). The only stationary points obtainable for triplet cyclopropenone correspond to A and C with the latter being the minimum. While similar geometries are also stationary points on the thione triplet surface, the only minimum corresponds to the structure analogous to the highly unsymmetrical F. Some of the unusual structural features of the minimum energy geometry, especially pyramidalization at a single carbon atom and the shortening of the opposite CC bond are thus found to have a simple electronic origin.

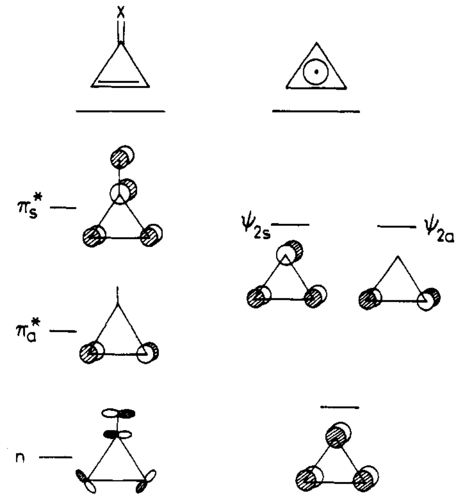

Figure 7. The nonbonding n orbital and the two π^* orbitals of cyclopropenethione and ketone. The π MO's of the cyclopropenyl system are given for comparison. Note the similarity within the pairs π_a^*, ψ_{2a} and π_s^*, ψ_{2s}.

The reason for the thione and ketone triplets to prefer alternative Jahn–Teller distorted forms can be traced to the orbital energy pattern in these systems. In the ground state, the LUMO of both cyclopropenethione and cyclopropenone is a pure π_{cc}^* orbital (π_a^* in Figure 7) with no contribution from the C=X fragment due to symmetry. A higher lying π^* orbital has considerable π_{cx}^* character. Due to similar electronegativities of carbon and sulfur,[14] π_a^* and π_s^* orbitals are nearly degenerate for the thione.

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(13) The existence of two nearly degenerate structures, one of which is a minimum and the other a pseudorotation transition state, seems to be characteristic of Jahn-Teller surfaces of annulene radicals, in general. See: Hobey, W. D.; McLachlan, A. D. *J. Chem. Phys.* **1960**, *33*, 1965. McConnell, H. M.; McLachlan, A. D. *J. Chem. Phys.* **1961**, *34*, 1. Van der Waals, J. H.; Berghuis, A. M. D.; de Grost, M. S. *Mol.. Phys.* **1967**, *13*, 301. Purins, D.; Karplus, M. *J. Chem. Phys.* **1975**, *62*, 320. Also see ref 12 and 19.

(14) Pauling, L. *The Nature of the Chemical Bond*; Cornell University: Ithaca, NY, 1960.

On the other hand, due to the differing stabilities of $\pi_{cc}{}^*$ and $\pi_{co}{}^*$ orbitals, the $\pi_s{}^*$ orbital in the case of cyclopropenone lies considerably higher in energy with several intervening ring σ^* orbitals. Therefore, the $n\pi^*$ triplet of cyclopropenone has an odd electron in the $\pi_a{}^*$ orbital with identical symmetry properties of the ψ_{2a} orbital of the cyclopropenyl system. As a result, the preferred structure corresponds to the allyl form (C). The near degeneracy of $\pi_a{}^*$ and $\pi_s{}^*$ for the thione leads to a greater variety of structures. Structures with $\pi_a{}^*$ occupancy have been obtained but correspond to transition states on the potential energy surface. The more stable geometry corresponds to an alternative form in which considerable mixing of $\pi_a{}^*$ and $\pi_s{}^*$ orbitals occurs through symmetry lowering.

To test the above electronic interpretation for the structural deformations in the $n\pi^*$ triplet state, additional calculations were performed on the radical anions of cyclopropenone and cyclopropenethione. In these ions, the number of π electrons is increased by one without modifying the σ framework. The structural changes can then be entirely attributed to the presence of five π electrons in these systems. The calculated structures, relative energies, and Hessian indices of the radical anions (Figure 3) parallel the results of the $n\pi^*$ triplet of the corresonding neutral molecules. The ketone radical anion adopts C_2 and C_s allylic geometries analogous to A and C. The corresponding structures are transition states in the case of the thione radical anion. An interesting C_s structure with sulfur bent significantly out of the ring plane is obtained during geometry optimization. However, this form is relatively less stable and has two negative eigenvalues in the force constant matrix. This structure is the enyl form with symmetric substitution (form E in Figure 6) and results from an odd electron in the $\pi_s{}^*$ orbital of Figure 7. The most stable geometry of the thione radical anion is the symmetrical enyl structure F with only one carbon having significantly pyramidal coordination. These results confirm the earlier analysis that many of the key features of the triplet geometries are entirely attributable to π interactions.

The role of σ interactions in producing additional structural deformations in the triplet state can be assessed by focusing on the differences in the geometries of the radical anion and the neutral triplet. The differences are fairly small in the case of the ketone. The additional perturbation in the π framework of the triplet reduces the CO bond length, lengthens the α-CC bonds and shortens the unique CC bond. All these changes are consistent with an attractive three-electron interaction in which one of the Walsh orbitals of the three-membered ring[15] donates electron density into the partly filled carbonyl n orbital (Figure 8). The corresponding interaction is destabilizing in the neutral system as well as in the radical anion due to the involvement of four electrons. For the thione, more drastic differences are found between the triplet and the radical anion, although the electronic origin is similar to that in the ketone. The π interactions produce an unsymmetrical ring symmetry to begin with, as seen from the radical anion geometry. Donation of electron density into the n orbital SOMO from the adjacent CC bonds is no longer symmetrical. Interaction involving the longer CC bond is energetically more favorable, leading to a further lengthening of that bond. Ultimately, the CC bond which shares the n orbital electron deficiency becomes especially long and a nearly linear CCS fragment is produced with a short CC bond.

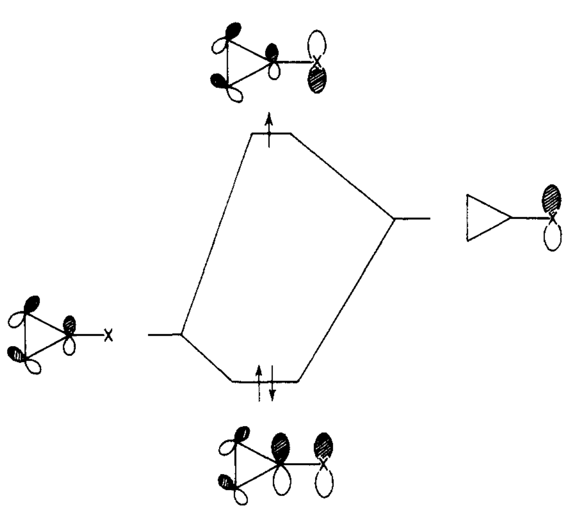

Figure 8. Interaction in the triplet state between the n orbital on X and the symmetric Walsh orbital of the adjacent three-membered ring.

In summary, the electronic charge distribution in $n\pi^*$ triplet cyclopropenethione is as follows. Of the five π electrons, four are delocalized over a CCS fragment, which thus resembles a thiaallyl group. The remaining π electron is localized at a pyramidal carbon. In the σ framework, the positive charge at the n_X orbital is selectively shared by the α-CC bond involving the pyramidal carbon.

Substituent Effects on Thione Triplet Geometries. The unsymmetrical geometry of triplet cyclopropenethione leads to two possible isomeric structures for substituted derivatives. Of the two carbon atoms which can bear a substituent, one is part of a delocalized thiaallyl group with four π electrons. The other is a pyramidal, localized radicaloid center. Substituents with stabilizing π interactions are expected to prefer the former location. Calculations on a few model systems confirm this expectation (Figure 4). Geometry optimization from a variety of initial geometries of monomethyl cyclopropenethione in the $n\pi^*$ triplet state leads to a single unsymmetrical structure. The favored geometry is remarkably similar to the unsubstituted triplet form with the methyl group interacting with the thiaallyl group by remaining nearly in the ring plane. The nonstabilizing hydrogen atom is at the pyramidal carbon which forms a long bond with the C_X atom. Calculations were also carried out on dimethylcyclopropenethione to establish that the basic structural preference is unaltered by multiple substitution. The preferred triplet has an unsymmetrical structure similar to the unsubstituted case.

Extrapolating these model calculations to the larger arylalkylcyclopropenethiones studied experimentally, the $n\pi^*$ triplet state is likely to have an unsymmetrical geometry in which the more stabilizing aryl group remains in the ring plane attached to the thiaallyl fragment. The alkyl group is expected to be at the pyramidal carbon, forming an elongated bond. Cleavage of that bond will then lead to the less stable thioketene carbene/diradical intermediate.

Conclusion and Outlook

The unusual regiochemistry observed for the α-cleavage of arylalkylcyclopropenethione is suggested to be determined by the preferred geometry of the reactant triplet. The more stable triplet isomer leads to the less stable thioketene carbene intermediate.

A similar explanation may apply for other photochemical reactions exhibiting unexpected regiochemistry. For example, photocleavage of unsymmetrically substituted cy-

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(15) Jorgensen, W. L.; Salem, L. *The Organic Chemists Book of Orbitals*; Academic: New York, 1973; pp 19–23, 154.

clopropene yields the less stable vinyl carbene, in contrast to the analogous thermal reaction.[16] In such cases the efficiency of funneling to the ground-state surface is usually held responsible for the observed products.[4,16] However, it is quite conceivable that triplet cyclopropene is unsymmetrical. Substituent effects on this structure may again determine the nature of the α-cleavage product. Interestingly, Johnson et al.[17] have recently considered an explanation other than that based on the funneling process. They have speculated that the π bond strength in the excited state may be reversed, leading to the difference between thermal and photochemical cleavage products. Our proposal is a variation of this suggestion. The results of the theoretical study initiated by Johnson et al. on cyclopropene chemistry are eagerly awaited.

The present calculations are not meant to be definitive, although the MINDO/3 method has been successfully used in earlier studies of photoreactions[18] and Jahn–Teller systems.[19] Our results merit further investigation at higher levels employing configuration interaction.[20]

The current study has yielded a variety of unusual substituted Jahn–Teller forms. The unsymmetrical structure F found for the triplet of the parent as well as substituted cyclopropenethione represents an especially interesting Jahn–Teller distorted geometry.

The alternative geometries adopted by triplet cyclopropenone and -thione represent a particularly striking example of orbital isomerism.[21] A systematic study of the effect of other substituents in preferentially stabilizing different "lumomeric" structures will be of considerable interest.

Acknowledgment. V.R. thanks the Department of Science and Technology, Government of India for financial support.

Registry No. 2-Methyl-3-phenyl-2-cyclopropene-1-thione, 56764-07-9; 2-ethyl-3-phenyl-2-cyclopropen-1-one, 5909-87-5; 3-phenyl-3-propyl-2-cyclopropene-1-thione, 97703-38-3; 2-(1-methylethyl)-3-phenyl-2-cyclopropene-1-thione, 97703-39-4; 2-cyclopropene-1-thione, 69903-36-2; 2-cyclopropen-1-one, 2961-80-0; cyclopropanol (anion), 72507-73-4; cyclopropanethiol (anion), 100840-42-4; 2-methyl-2-cyclopropene-1-thione, 103422-48-6; 2,3-dimethyl-2-cyclopropene-1-thione, 103422-49-7.

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[17] Klett, M. W.; Johnson, R. P. *J. Am. Chem. Soc.* **1985**, *107*, 3963.

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[19] Bischof, P. *J. Am. Chem. Soc.* **1977**, *99*, 8145. Clark, T.; Chandrasekhar, J.; Schleyer, P. v. R.; Saunders, M. *J. Chem. Soc., Chem. Commun.* **1980**, 265.

[20] A quantitative theoretical treatment of Jahn–Teller systems should include extensive configuration interaction. See Ref 10c and: Borden, W. T.; Davidson, E.; Feller, D. *J. Am. Chem. Soc.* **1980**, *102*, 5302.

[21] Dewar, M. J. S.; Kirschner, S.; Kollmar, H. W. *J. Am. Chem. Soc.* **1974**, *96*, 5240.

Diastereoselective Synthesis of Chiral Secondary Amines with Two Chiral Centers Directly Attached to the Nitrogen Atom

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Received January 12, 1986

The synthesis of the amines **1a–f** by hydrogenation of the corresponding imines **4a–f** occurs with a diastereoselectivity ranging from 33% to higher than 90%. The absolute configurations of **1b–f** have been determined by either X-ray analysis (**1b** and **1c**), chemical correlation (**1e** and **1f**), or correlation via ^{1}H NMR shifts (**1d**). The difference in the observed diastereoselectivities is rationalized by a mechanism in which the hydrogenation occurs exclusively at the less hindered side of the imines, which results in the formation of amines **1** from the anti and of amines **2** from the syn imines.

Chiral amines constitute a class of compounds that have a wide application in organic chemistry as resolving agents[1] and chiral building blocks,[2] as well as chiral auxiliaries in stereoselective synthesis.[3] Naturally occurring amines such as brucine, ephedrine, and amino acids, as well as synthetic amines such as α-methylbenzylamine and 2-amino-1-butanol, are frequently used. An advantage of the use of natural chiral amines is that they occur in an optically pure form, while for the synthetic amines a resolution procedure or a stereoselective synthesis is necessary. However, a drawback of the first class is that they often are only available in one enantiomeric form.

The most successfully used method of synthesis of chiral amines involves hydrogenation of imines, in which the chiral center can be induced in various ways.[4-9] However, for the synthesis of amines with two chiral centers directly attached to the nitrogen atom the preferred method consists of condensation of prochiral ketones with chiral primary amines to afford chiral imines, which after hydrogenation yield secondary amines, possessing tow chiral centers.[6] Although a great deal of work has been done on this type of reaction it has mostly been restricted to the

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[1] See, for example: Wilen, S. H. in *Topics in Stereochemistry*; Allinger, N. L., Eliel, E. L., Eds.; Wiley-Interscience: New York, 1971; Vol. 6, pp 107–176.

[2] See, for a review about amino acids as chiral building blocks: Drausz, K.; Kleeman, K.; Martens, J. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 584.

[3] See, for example: Valentine, D.; Scott, J. W. *Synthesis* **1978**, 347.

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[5] Levi, A.; Modena, G.; Scorrano, G. *J. Chem. Soc., Chem. Commun.* **1975**, 6.

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