JOC Article

Triplet Photochemistry of Vinyl Cyclopropenes: Mechanistic and Exploratory Organic Photochemistry[1,2]

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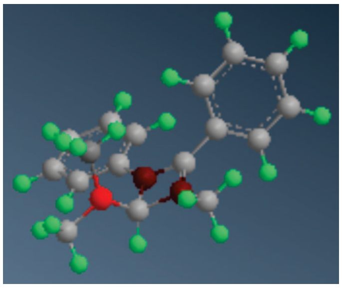
Received October 14, 2008



Our research on the triplet photochemistry of vinylcyclopropenes has dealt with a diverse series of systems, providing a series of experimental examples and mechanstic studies. It perhaps is not surprising that the reaction mechanisms have been controversial. The present study is theoretical and provides evidence for control by a critical T_1 diradical intermediate which has a high spin−orbit coupling with S_0 ground-state along the mechanistic pathway. The evidence now for the one pathway derives from independent generation and behavior of this diradical, prediction of the reaction regioselectivity in nine diverse examples, the S_0 and T_1 hypersurfaces in the reaction, and an S_0-T_1 degeneracy with SOC for the critical diradical. This triplet diradical when independently generated gives the same regioselectivity observed in examples starting with the vinylcyclopropene triplet itself. The overall reaction provides a useful synthesis of cyclopentadienes.

Introduction

Our research uncovered the triplet (i.e., sensitized) rearrangement of vinylcyclopropenes to afford cyclopentadienes.[3a−e] We considered four reaction mechanisms, **A**, **B**, **C**, and **D**. Mechanism **C** is unique in being in accord with product structures in nine cases.[3e] Common to all examples is a cyclobutenylcarbinyl diradical **C′** appearing midway in the reaction sequence (note that the intermediates are labeled with a prime). The evidence is complex, based on organic reaction results and mechanistic reasoning, but quite conclusive. However, the proposed mechanism has been severely criticized. Su has stated that our "predictions are not consistent with experimentally observed behavior"[4,5] and has proposed an alternative mechanism. The basis for this alternative consisted of a novel qualitative comparison of algebraic expressions for spin−orbit (SOC) coupling with selected truncated organic structures. With that approach, it was concluded that SOC was largest in the last stage of the reaction. And, intermediate **C′** was not included in the mechanism.[4]

Lacking was computational support for the mechanism. Thus, one item needed was explicit computations of energy and spin−orbit coupling at different points along the reaction coordinate. The present study provides these along with consideration of the structural evidence which includes independent generation of the critical intermediate **C′** (**3**, vide infra).

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(1) This is paper 192 of our photochemical series and paper 285 of our general series.

(2) For papers 282−284, see: (a) Zimmerman, H. E. *Pure Appl. Chem.* **2006**, 2193–2203. Porter Award Address: (b) Zimmerman, H. E.; Mitkin, O. D. *J. Org. Chem.* **2007**, *72*, 6091–6096. (c) Zimmerman, H. E.; Suryanarayan, V. *Eur. J. Org. Chem.* **2007**, 4091–4102.

(3) (a) Zimmerman, H. E.; Aasen, S. *J. Am. Chem. Soc.* **1977**, *99*, 2342–2344. (b) Zimmerman, H. E.; Hovey, M. C. *J. Org. Chem.* **1979**, *44*, 2331–2345. (c) Zimmerman, H. E.; Kreil, D. J. *J. Org. Chem.* **1982**, *37*, 2060–2075. (d) Zimmerman, H. E.; Fleming, S. A. *J. Am. Chem. Soc.* **1983**, *105*, 622–624. (e) Zimmerman, H. E.; Fleming, S. *J. Org. Chem.* **1985**, *50*, 2539–2551.

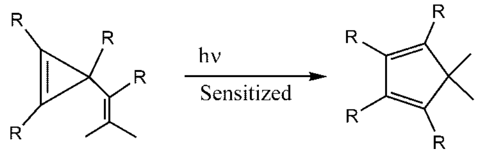
(4) (a) Su, M.-D. *Tetrahedron* **1995**, *51*, 5871–5876. (b) Su, M.-D. *J. Chem. Theory Comput.* **2008**, *4*, 1263–1273.

(5) (a) This point contrasts with the statement by Su (ref 4a) that the four mechanisms (A−D) have been adopted to explain the vinylcyclopropene chemistry). In our work, we have considered all four only as a priori possibilities. For example, it is known that carbenes are formed from cyclopropene excited singlets but not triplets but carbenes were said to be adopted in our proposed mechanisms. (b) While the several mechanisms were considered in our very early studies, mechanism C had become especially clear near the end (ref 3b) and was established in ref 3d.

10.1021/jo802313r CCC: $40.75

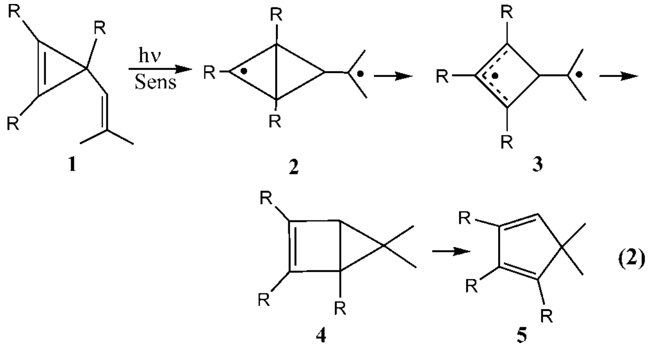
The Photochemical Evidence

The rearrangement of vinylcyclopropenes to afford cyclopentadienes on sensitized photolysis[3a] is illustrated in eq 1. In Table 1 there are six of our earlier rearrangements whose mechanism needed understanding while in Figure 1 there are intermediate structures for four conceivable mechanisms, **A**, **B**, **C**, and **D**. The four are applied to the second example in Table 1 with one reaction intermediate (**A′**, **B′**, **C′**, **D′**, respectively) illustrated in Figure 1 for each pathway. At this point, only the structural features are being considered; the reaction multiplicity and computational results are discussed below. Suffice it to say that, although three of these intermediates, **A′**, **B′**, and **D′**, prove consistent with individual cases, they do not lead to all six of the product structures.



(1)

In contrast, reaction mechanism **C** is in accord with all of the six examples. The complete pathway is outlined in generic form in eq 2. Diradical **3** (**C′**) turns out to be a species common to all examples and a species critical to the reaction. Hence, one basic error by Su[4] was the statement that our proposed mechanism was not consistent with our experimental results. Another basic error by Su was that his theoretical considerations[4] did not include the critical Diradical **C′**, a point to be considered below.



(2)

Chart 1 illustrates the reactivity[3e] of three vinylcyclopropenes, **6**, **10**, and **14**. Starting with vinylcyclopropene **6**, two photoproducts **8** and **9** are obtained. Beginning with vinylcyclopropene **14**, two of the four photoproducts are the same two (i.e., **8** and **9**) and obtained in the same ratio. Similarly, beginning with vinylcyclopropene **10**, cyclopentadienes **12** and **13** result; these are the other two photoproducts obtained beginning with vinylcyclopropene **14**. Again, the ratio of products is the same as from a different reactant, i.e., **10**. The common and critical feature which accounts for this behavior is the intermediacy of a common mechanism **C** diradical (i.e., **7**) in eqs 9a and 10a as well as **11** in eqs 9b and 10b in Chart 1.

Especially convincing is the sensitized photolysis of azobicyclic **15** (note eq 11) to afford the critical diradical **7** (i.e., a mechanism **C** species).[3e] This again leads to cyclopentadienes **8** and **9** and in the same ratio as seen in reactions 9a and 10a (Chart 1).

Computational Results

For simplicity, computations were run on the triphenylvinylcyclopropene **16** but with both density functional b3lyp and CAS-SOC as embodied in Gaussian 2003 and with a basis set of 6-31G(d). The computations were run on S_0 and T_1 for the five species **16**−**20** as depicted in eq 12. Note Table 2. Finally, an MP2 computation was performed to ascertain whether it was the correlation energies which account for the DFT computations being of lower energy. The data are plotted in Figures 2 and 3 for the two types of computations, DFT and spin−orbit coupling.

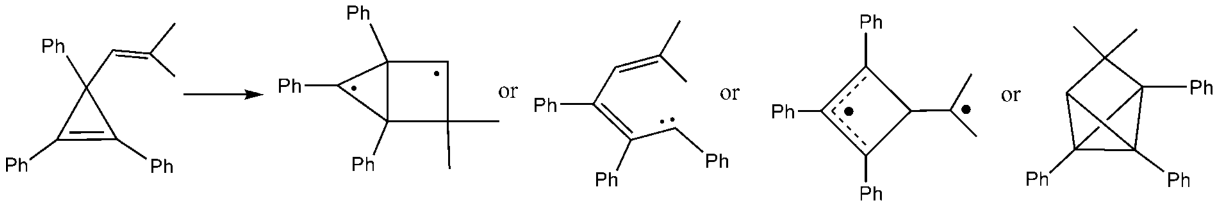
Discussion

We first note that our proposed mechanism C accounts for the structural and regioselective features all of the nine known triplet rearrangements of 1-vinylcyclopropenes to afford cyclopentadienes — those in eqs 1−8 as well as in equations 9a, 9b, 10a and 10b. This contrasts with the statement of Su.[4,5] It is critical that we recognize that this T_1 triplet reactivity of vinylcyclopropenes is distinguished from S_1 photochemistry. Related to this, in our original analysis were four reasonable mechanisms, three of which are compatible with individual examples but not with all. Additionally, in most of our earlier studies we included singlet photochemistry from direct irradiations.[3a−e] However, it has been clear from the outset that the triplet reactivity is quite different from that of the excited singlet.

While the preference for mechanism C seemed initially seemed clear,[3a−d] it is the reactivity of vinylcyclopropenes **6**, **10**, and **14** which is most convincing. Thus, mechanism C cyclobutenyl diradical **7** is common to two different vinylcyclopropene reactants, **6** and **14**. Similarly, cyclobutenyl diradical **11** is common to the reactions of **10** and **14**. In both instances, the same cyclopentadiene product ratio results.

The independent generation of the cyclobutenyl diradical **7** from azobicyclic **15** leads to the same two cyclopentadienes, **8** and **9**, as seen in the vinylcyclopropene triplet photochemistry of **6** and **14**.

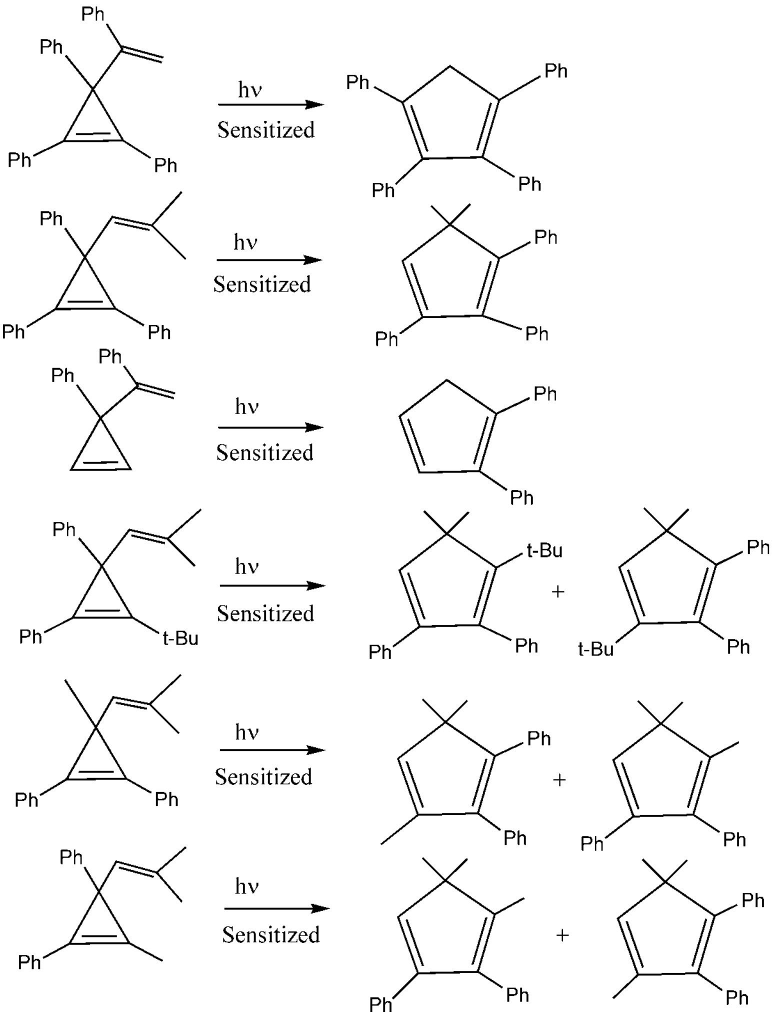
What has been discussed thus far is the “organic chemist’s mechanistic approach”. Lacking has been a true computational description of the reaction. The publication of Su utilized a



Mech A (A') **Mech B (B')** **Mech C (C')** **Mech D (D')**

FIGURE 1. Four possible intermediates applied to the example in eq 4 in Table 1.

TABLE 1. Six Examples of Vinylcyclopropene Rearrangements



(3)

(4)

(5)

(6)

(7)

(8)

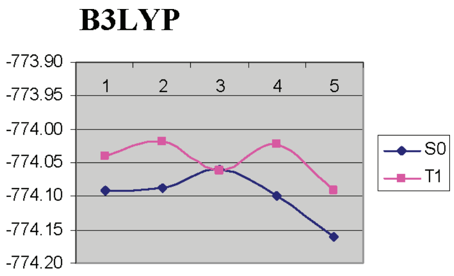


FIGURE 2. Plot of DFT energies for S0 and T1 for stages 1−5 (corresponding to compounds **16**, **17**, **18**, **19**, and **20**).

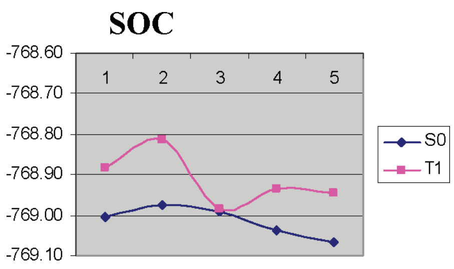


FIGURE 3. Plots of spin−orbit coupling energies for S0 and T1 for stages 1− 5 (corresponding to compounds **16**, **17**, **18**, **19**, and **20**).

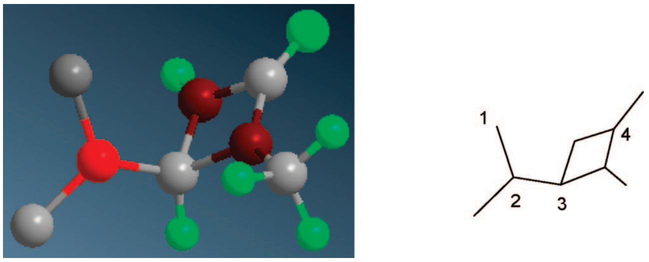
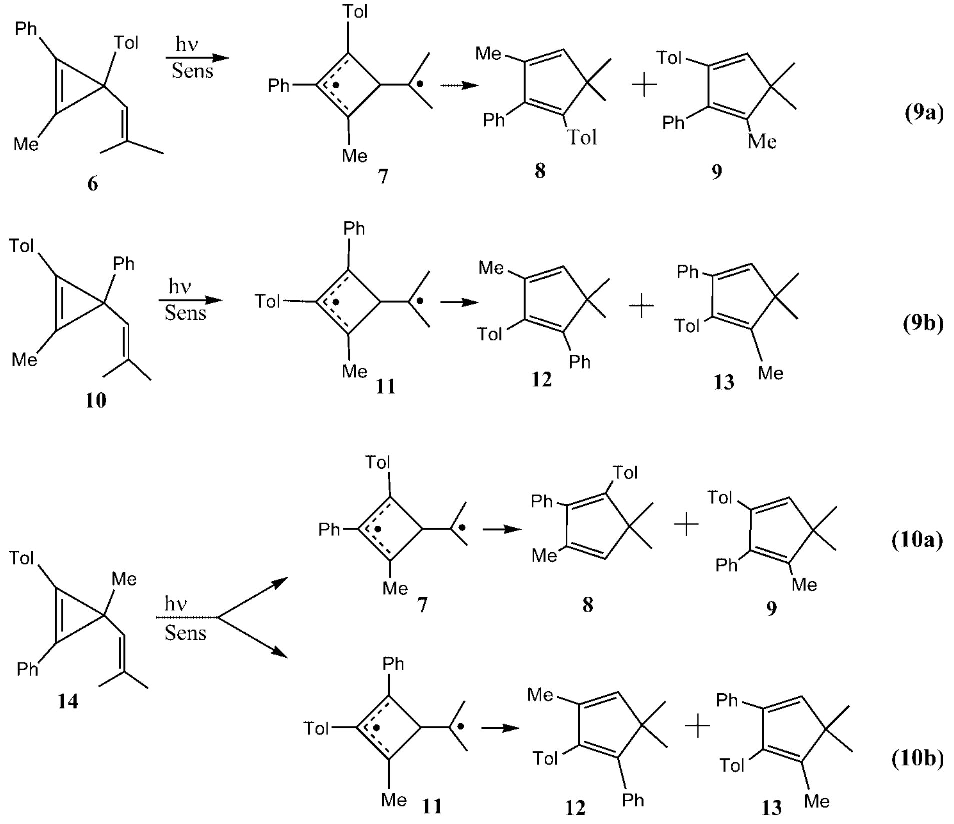


FIGURE 4. Chem 3D picture of the critical cyclobutenyl carbinyl diradical **C′** (truncated).

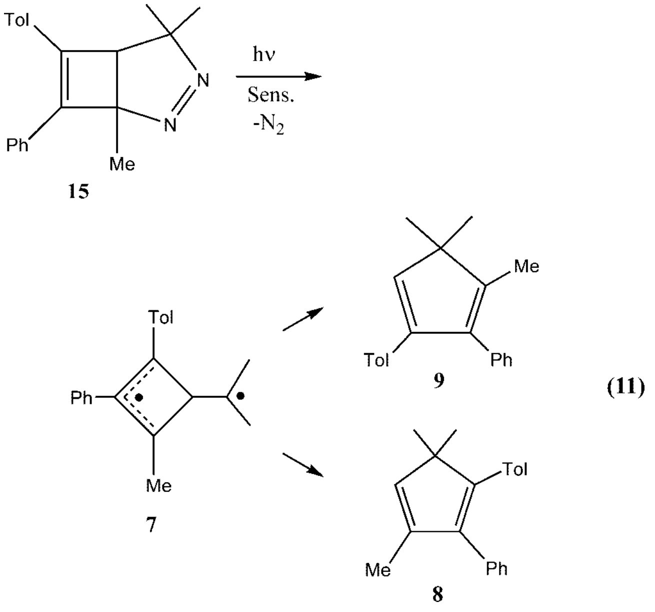
qualitative application of algebraic predictions of T1-S0 spin−orbit coupling of the reacting species. However, this alternative mechanism proposed by that author did not include the cyclobutenylcarbinyl diradical. Rather, it offered a concerted rearrangement in which, in the last step, the triplet housene species (**4** in equation 2) was considered to undergo a rate-limiting disrotatory opening effected by spin−orbit coupling.

It is correct that a disrotatory opening is required by the small ring size for reasons of ring-strain. In S_0, a four-electron disrotatory electrocyclic ring opening is formally forbidden.[6,7] However, it is known[8,9] that housene isomerizes to cyclopentadiene at room temperature.

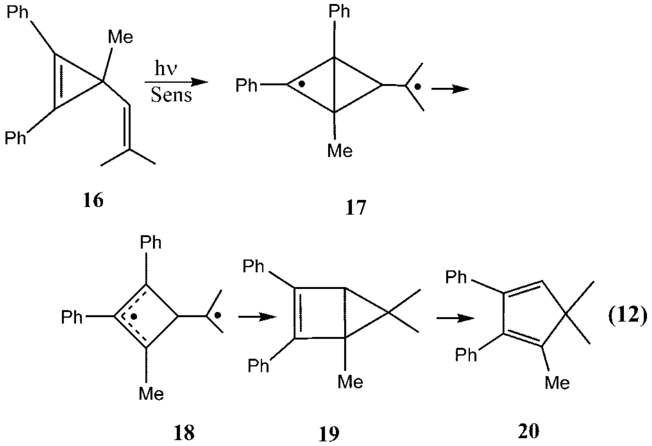
CHART 1. Common Cyclobutenyl Dicarbinyl Intermediates in Three Reactions



This is a consequence of large ring strain. With aryl groups conjugated to the π system and lack of symmetry, the isomerization should be even more facile in the housene to cyclopentadiene S_0 steps of the present systems. Computational evidence is not available for a triplet disrotatory opening.



More cogent are the computational results as outlined in Table 2 and Figures 2 and 3. The CASSCF spin−orbital computations reveal that the maximum coupling is exhibited by the Cyclobutenyldicarbinyl Diradical **C′**. Perhaps more visual and obvious are the two plots (Figures 2 and 3) of T_1 and S_0 energies versus transformation of vinylcyclopropene to cyclopentadiene for the example shown in eq 12. It is seen that as the cyclobutenyldicarbinyl triplet **18T** is reached, there is a degeneracy with touching of the T_1 and S_0 surfaces. Facile conversion to ground-state S_0 is anticipated, and the remainder of the reaction course should then be on the ground-state surface.



Finally, in Figure 4 we show the critical cyclobutenyl diradical **C′** in three dimensions but truncated with the two phenyl groups replaced by hydrogens to permit facile inspection. The odd-

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(8) Golden, D. M.; Brauman, J. I. *Trans. Faraday Soc.* **1969**, *65*, 464–469.

(9) Roth, W.; Klaerner, F.-G.; Lennartz, H.-W. *Chem. Ber.* **1980**, *113*, 1818–1829, and references cited therein.

TABLE 2. **b3lyp and SOC Computations**[a–d]

16	17	18	19	20	
b3lyp computations					
−774.040616	−774.0189247	−774.061220	−774.023064	−774.091473	T1
−774.090715	−774.0872293	−774.060592	−774.098401	−774.159916	S0
spin−orbit					
−768.883484	−768.8127037	−768.9842497	−768.9342749	−768.9469053	T1
−769.005872	−768.9747699	−768.9930104	−769.0371672	−769.0676734	S0
0.3 cm^{-1}	0.4 cm^{-1}	1.0 cm^{-1}	0.9 cm^{-1}	0.1 cm^{-1}	SOC

[a] The CASSCF-SOC computations do not include core correlation effects (e.g., 2.684236904 hartree for **16**). [b] The last line of the SOC table gives spin−orbit coupling values. [c] For the last two steps, only one of the two closures of **18** is given as representative. [d] Note: 627.5 kcal/mol per hartree.

electron carbonyl carbon (bright red) bonds to one of the maroon allylic carbons to form the bicyclic housene intermediate. The 1−2−3−4 dihedral angle is 20.1°, which then has the odd-electron, carbinyl p-orbital bissecting the four-ring allylic π-system in a Hückel array. In simplistic terms, this leads to a HOMO−LUMO degeneracy, surprisingly in accord with the much more sophisticated computations.

Conclusion

The evidence for the triplet vinylcyclopropene rearrangement to cyclopentadienes seems conclusive. The algebraic considerations of Su erred minimally in not considering diradical **C′** which actually undergoes the intersystem crossing. Some related important aspects are suggested by the present author. One is that the first step in determining mechanisms, in general, is consideration of the experimental organic behavior. The second is that theoretical conclusions based on truncated structures, lacking potentially critical substituents, tend to lead to conclusions not consistent with reality.[10]

Acknowledgment. Support of this research by the National Science Foundation is gratefully acknowledged with special appreciation for its support of basic research.

Supporting Information Available: Computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) This point was prompted by a parallel situation (e.g., ref 2c) dealing with the many mechanisms in our past research in which zwitterions play an important role.