Ab Initio Study of Hydrogen Abstraction by Triplet Cyclopropylidene and Planar Triplet Allene

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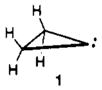
Cyclopropylidene (1, $^3B_2$) and bent planar allene (2, $^3A_2$) are low-energy minima on triplet C_3H_4 potential energy surfaces. Hydrogen abstraction by intermediates 1 and 2 may be an important process in the triplet photochemistry of allenes. Ab initio calculations at the UMP3/6-31G*//UHF/3-21G level are reported for hydrogen abstraction from methane by triplet 1 and 2. In both cases, predicted saddle point geometries have the abstracted hydrogen coplanar with the four carbon atoms. The calculations predict E_a = 16.7 and 18.8 kcal/mol for abstraction by 1 and 2, respectively, with corresponding heats of reaction of −4.14 and −3.60. Abstraction by 1 is remarkably insensitive to out-of-plane hydrogen deformation at the saddle point, while reaction of 2 is much more sensitive to geometry. Attempts are made to locate other triplet C_3H_4 minima with MCSCF or UHF wavefunctions. Implications for allene photochemistry are discussed.

Introduction

Hydrogen atom abstraction is a common reaction of triplet excited states and odd electron species, such as carbenes and radicals.[1,2] Triplet-excited-state photoreactions of simple allene (1,2-propadiene) derivatives are characterized predominantly by intramolecular hydrogen abstraction at proximate C–H bonds.[3-7] These reactions were first investigated during the 1960's by Ward and Karafiath, who proposed two intermediates: triplet cyclopropylidene (1) and planar triplet allene (2).[4] These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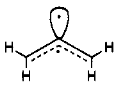
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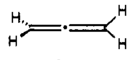
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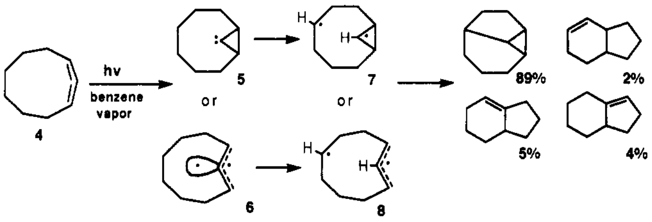
can result from allene (3) through either π bond rotation and closure or rotation and bending, respectively. In the well-studied case of 1,2-cyclononadiene (4, Scheme I), intramolecular hydrogen abstraction by either 5 or 6 can lead to the observed products.[4,6]

Allene triplet states usually are generated by benzene sensitization.[3-7] Allene T_1 and T_2 (4.3 and 4.9 eV[8]) lie above the 3.66-eV triplet energy of benzene; energy transfer to allene must be "nonvertical".[9] Thus, 1 and 2, which are lower energy (ca. 3.4 and 2.2 eV, respectively) minima on the triplet C_3H_4 surface,[6] are logical intermediates in these reactions.

Cyclopropylidenes have resisted matrix isolation attempts and remain relatively poorly characterized among carbenes.[10] Singlet 1 is predicted to undergo ring opening to allene, with a barrier of 12–14 kcal/mol.[11] The ground-state multiplicity of 1 is not known from experiment, but recent ab initio studies predict a singlet ground state, with a singlet–triplet gap of 12–15 kcal/mol.[6,11] For allene, π bond rotation results in a planar triplet 2, which has been predicted to have a bent structure[12] and to lie ca. 1 eV below triplet 1.[6,11b] This diradical is electronically similar to a triplet carbene, except that the π nonbonding orbital will have a node at C-2. MCSCF calculations on diradical 2 predict a singlet ground state, with a singlet–triplet gap of 4.8 kcal/mol.[13] This small singlet–triplet gap undoubtedly contributes to a short lifetime for 2. Ab initio calculations predict a 23.7 kcal/mol barrier for opening of triplet 1 to 2.[11b]

Scheme I. Photochemistry of 1,2-Cyclononadiene



Experimental studies indicate that reaction mechanisms are quite dependent on structure.[3-7] In the case (Scheme I) of 1,2-cyclononadiene,[4,6] we have isolated minor reaction products that seem best derived from a common 1,3-biradical; this implies late formation of the three-membered ring and hydrogen abstraction by 6 rather than 5. Other acyclic examples do not require cyclopropylidene formation.[4,5] Our own recent studies on a *tert*-butyl-1,2-cyclooctadiene also argue against a cyclopropylidene.[7b] Compelling evidence *for* a triplet cyclopropylidene is provided by the reactions of 1,2-cyclodecadiene.[7a] In this case, the

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[1] For reviews and leading references, see: (a) Platz, M. S. *Acc. Chem. Res.* **1988**, *21*, 241. (b) Tedder, J. M. *Tetrahedron* **1982**, *38*, 313. (c) Wentrup, C. *Reactive Molecules: The Neutral Reactive Intermediates in Organic Chemistry*; John Wiley and Sons: New York, 1984.

[2] For other theoretical studies on hydrogen abstraction reactions, see: (a) Wildman, T. A. *Chem. Phys. Lett.* **1986**, *126*, 325. (b) Severance, D.; Pandey, B.; Morrison, H. *J. Am. Chem. Soc.* **1987**, *109*, 3231. (c) Gordon, M. S.; Gano, D. R.; Boatz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 5771. (d) Gordon, M. S. *J. Am. Chem. Soc.* **1984**, *106*, 4054. (e) Bauschlicher, C. W., Jr.; Bender, C. F.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1976**, *98*, 3072. (g) Carr, R. W. *J. Phys. Chem.* **1972**, *76*, 1581. (h) Bodor, N.; Dewar, M. J. S.; Wasson, J. S. *J. Am. Chem. Soc.* **1972**, *94*, 9095.

[3] Review: Johnson, R. P. *Org. Photochem.* **1985**, *7*, 75.

[4] Ward, H. R.; Karafiath, E. *J. Am. Chem. Soc.* **1969**, *91*, 522.

[5] Karan, H. I. *J. Org. Chem.* **1981**, *46*, 2186.

[6] (a) Stierman, T. J.; Johnson, R. P. *J. Am. Chem. Soc.* **1985**, *107*, 3971. (b) Stierman, T. J.; Shakespeare, W. C.; Johnson, R. P. *J. Org. Chem.* **1990**, *55*, 1043.

[7] (a) Price, J. D.; Johnson, R. P. *J. Am. Chem. Soc.* **1985**, *107*, 2187. (b) Price, J. D.; Johnson, R. P. *J. Org. Chem.*, previous paper in this issue.

[8] Mosher, O. A.; Flicker, W. M.; Kupperman, A. *J. Chem. Phys.* **1975**, *62*, 2600.

[9] (a) Schmidt, M. W.; Lee, E. K. C. *J. Am. Chem. Soc.* **1970**, *92*, 3579. (b) Rodriguez, O.; Morrison, H. *J. Chem. Soc., Chem. Commun.* **1971**, 679.

[10] (a) Jones, M., Jr.; Moss, R. A. *Carbenes*; John Wiley & Sons; 1973, 1975; Vols. I and II. (b) For an excellent recent review of cyclopropylidene chemistry, see: Backes, J; Brinker, U. H. *Houben Weyl, Methoden der Organischen Chemie*; Georg Thieme Verlag; Stuttgart, 1989; Band E19b, p 391.

[11] (a) Valtazanos, P.; Elbert, S. T.; Ruedenberg, K. *J. Am. Chem. Soc.* **1985**, *107*, 3780; *Theor. Chim. Acta* **1986**, *69*, 281. (b) Rauk, A.; Bouma, W. J.; Radon, L. *J. Am. Chem. Soc.* **1985**, *107*, 3780. (c) Honjou, N.; Pacansky, J.; Yoshimine, M. *J. Am. Chem. Soc.* **1985**, *107*, 5332. (d) Valtazanos, P.; Elbert, S. T.; Ruedenberg, K. *Theor. Chim. Acta* **1986**, *69*, 281. See also ref 6a for earlier calculations on cyclopropylidene.

[12] (a) Seeger, R.; Krishnan, R.; Pople, J. A.; Schleyer, P. V. R. *J. Am. Chem. Soc.* **1977**, *99*, 7103. (b) Krogh-Jespersen, K. *J. Comput. Chem.* **1982**, *3*, 571.

[13] Angus, R. O., Jr.; Schmidt, M. W.; Johnson, R. P. *J. Am. Chem. Soc.*, **1985**, *107*, 532.

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Table I. Summary of Computational Results

	total energies (hartrees)[a]			
species	HF/3-21G	HF/6-31G*	MP2/6-31G*	MP3/6-31G*
1 ($^3B_2$)	-115.11324	-115.76955	-116.10973	-116.13496
2 ($^3A_2$)	-115.17110	-115.81588	-116.14067	-116.17170
CH_4	-39.97688	-40.19517	-40.33242	-40.34844
CH_3	-39.34261	-39.55899	-39.66864	-39.68448
11	-115.82304	-116.46807	-116.80960	-116.84144
9	-115.75660	-116.41500	-116.77686	-116.80552
SP1[b]	-155.05734	-155.92735	-156.41481	-156.45673
SP2	-155.11162	-155.97056	-156.44504	-156.49017
12 ($^3A'$)	-115.14252	-115.78737	-116.10044	-116.13281

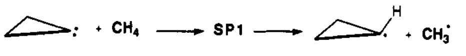
[a] All calculations employed RHF or UHF wavefunctions and geometries optimized with the 3-21G basis set. [b] SP1 and SP2 are saddle points. See Figure 2.

Table II. Summary of Reaction Energetics (kcal/mol)

level of calculation	predicted activation energy		reaction energies	
	SP1	SP2	eq 1	eq 2
UHF/3-21G	20.6	22.8	-5.7	-11.1
UHF/6-31G*	23.5	25.4	-5.8	-10.5
MP2/6-31G*	16.0	17.6	-3.2	-3.2
MP3/6-31G*	16.7	18.8	-4.1	-3.6

remarkable array of strained tricyclic products seems most consistent with stepwise reaction and initial three-membered-ring formation. What is puzzling about this reaction is its low selectivity, which implies minimal geometric requirements for hydrogen abstraction.

We describe here the results of ab initio calculations on the hydrogen abstractions depicted in eqs 1 and 2. Our goals were to determine the relative activation energies for these fundamental reactions, the saddle point geometries (SP1 and SP2), and their sensitivity to approach angle of the hydrogen.



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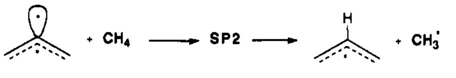

(2)

Computational Methods

Hartree–Fock (UHF and RHF) and Moller–Plesset calculations were performed with a standard VAX version of GAUSSIAN 82.[14] Most calculations reported are at the UMP3/6-31G*//UHF/3-21G level.[15] Geometries were optimized within appropriate symmetry constraints. Multiconfiguration SCF (MCSCF) calculations were performed with GAMESS.[16]

Geometries for triplets, doublets, and saddle points were taken from UHF/3-21G calculations. A final single-point calculation was then performed at the MP3/6-31G* level.[15] Geometric data for reactants (1, 2, and CH_4) and products (9–11) were either taken from or agreed well with previous calculations.[17] Methyl (10) and allyl (11) radicals are predicted to have planar, symmetrical structures, while cyclopropyl (9) is pyramidalized[17a] (38° out of plane bending at C-1) with a low barrier to planarity.[18] Triplet species 1 and 2 are predicted to be bent by 63.4° and 137.4° respectively. Saddle points for hydrogen abstractions were located approximately by initial reaction path calculations and then more rigorously characterized as points having a single imaginary frequency.

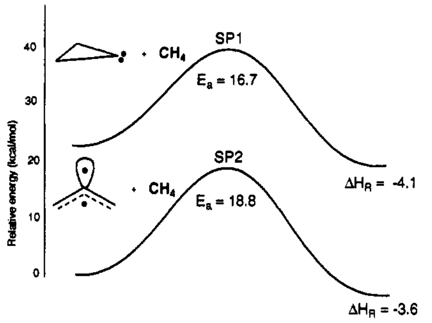

Figure 1. Energetics (kcal/mol) predicted from UMP3/6-31G* calculations.

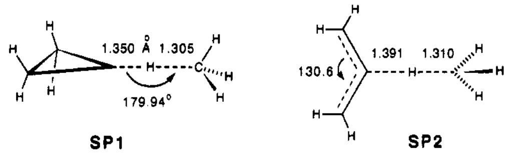

Figure 2. Predicted saddle point geometries from UHF/3-21G calculations.

Results of Calculations

Total energies for reactants, products, and saddle points are summarized in Table I. Relative reaction energetics and schematic potential energies curves at the UMP3/6-31G*//3-21G level are depicted in Figure 1. Table II provides a summary of calculated activation energies and reaction energies.

The saddle point structures for these two hydrogen abstractions are shown in Figure 2. Both are predicted to be linear, with the abstracted hydrogen and four carbon atoms essentially coplanar. As indicated by the relative C–H distances, the saddle points lie slightly closer to reactants than products. This is consistent with the modest predicted exothermicities.

Discussion

At the highest computational level employed, predicted barriers for hydrogen abstraction are 16.7 kcal/mol for triplet cyclopropylidene (eq 1) and 18.8 for planar triplet allene (eq 2). Abstraction of a secondary hydrogen, as in cyclic allene 4, should diminish this barrier by 2–3 kcal/mol. Gordon has recently reported a very comparable barrier of 17.9 kcal/mol for hydrogen abstraction (eq 3) by triplet methylene.[2d] In one earlier study, Schaefer and

$$^3CH_2: + CH_4 \longrightarrow 2\ CH_3^{\bullet} \qquad (3)$$

co-workers predicted a barrier of 18–23 kcal/mol for this reaction.[2e] BEBO[2f] and MINDO/2[2g] methods afford predicted barriers of 25.6 and 3.8 kcal/mol, respectively. Predicted and experimental values for hydrogen abstraction by simple alkyl radicals (e.g., $CH_3^{\bullet} + CH_4$) are generally 10–20 kcal/mol.[1,2] Our predicted activation energies are probably too high by several kcal/mol.

On the basis of our calculations, we conclude that the reactions in eqs 1 and 2 should have comparable activation energies and exothermicities and will follow essentially parallel surfaces. Both are predicted to have a linear transition state.

Saddle point geometries such as these are of fundamental interest, but we believe that more *chemical* significance should attach to their sensitivity to geometric distortion. Intramolecular hydrogen abstraction in 4 or

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[14] Binkley, J. S.; Frisch, M.; Roghavachari, K.; DeFrees, D. J.; Schlegel, H. B.; Whiteside, R.; Fluder, E.; Seeger, R.; Pople, J. A GAUSSIAN 82; Carnegie-Mellon University, Pittsburgh, PA.

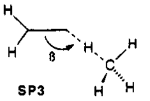
[15] Hehre, W. J.; Radom, L.; Schleyer, P. V. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley Interscience: New York, 1986.

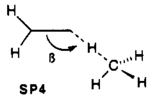
[16] Dupuis, M.; Spangler, D.; Wendoloski, J. J. NRCC Software Catalog, Vol. 1, program CG01, GAMESS, 1980; modified by Schmidt, M. W.; Elbert, S. T.; Lam, B., 1987.

[17] (a) Dupuis, M.; Pacansky, J. *J. Chem. Phys.* **1982**, *76*, 2511. (b) Gordon, M. S.; Gano, D. R.; Boatz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 5771.

[18] Walborsky, H. M. *Tetrahedron* **1981**, *37*, 1625.

1,2-cyclodecadiene[7a] must proceed through a substantially nonlinear geometry. Estimates of saddle point "flexibility" are available for 1 and 2. Initial attempts to locate the saddle point for 1 with a UHF/STO-3G wavefunction gave two geometries, SP3 and SP4, both with β = ca. 150°.

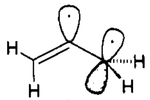

SP3


SP4

With the 3-21G basis set, both SP3 and SP4 collapsed to the linear SP2 geometry, however, both were only 1.3 kcal/mol (UHF/3-21G) higher than SP1. This result indicates that *substantial out-of-plane bending will have a very small effect on the saddle point energy.* Indeed, entropic differences might cancel these small differences in enthalpy. As a consequence, intramolecular hydrogen abstraction or abstraction in matrices may be insensitive to modest geometric changes. We are exploring the generality of this observation for other triplet carbenes. For planar triplet allene (2), we performed similar calculations in which β was systematically varied while the C1–H distance was fixed at the SP2 value. At the UHF/3-21G//STO-3G level, relative energetics were as follows: β = 180°, 0.0 kcal/mol; 170°, 1.6; 160°, 5.3; 150°, 10.6; 140°, 25.1. These data indicate that hydrogen abstraction by 2 should be much more sensitive to geometry. These differences presumably arise because the half-filled out-of-plane orbital in 1 is concentrated at C1, while in 2, there is a node at this site.

Predicted activation and reaction energies (Table II) are not strongly dependent on the level of calculation. It is remarkable that the HF/3-21G calculation compares well to UMP3/6-31G*, which requires ca. 50 times the computational effort for a single point.

One additional question is the existence of other triplet C_3H_4 species. We conducted a limited search using triplet MCSCF or UHF wavefunctions. Intermediates with D_{2h}, D_2, or C_2 symmetry all collapsed to 2. In addition to π bond twisting ($D_{2d} \rightarrow C_2$ or $D_{2d} \rightarrow D_2$), inplane bending ($D_{2d} \rightarrow C_s$) leads to substantial stabilization of the lowest triplet state of allene.[19] MCSCF or UHF geometry optimization, with restriction to C_s symmetry, gives a $^3A'$ species, best characterized as 12. Energetics of this species


12

are summarized in Table I. This structure is 18–24 kcal/mol above 2, and UHF/3-21G vibrational analysis gave a single imaginary frequency. We thus conclude that 12 is a saddle point for rotation of 2, rather than an intermediate. Martin, Yates, and Csizmadia recently reported calculations on a $^3A''$ (C_s) allene triplet state; this is predicted to be much higher energy than 12 and hence seems an unlikely intermediate.[20] We find no computational evidence for low-energy triplet C_3H_4 intermediates other than 1 and 2.

Conclusions

Hydrogen abstractions by triplet cyclopropylidene (1) and planar triplet allene (2) are predicted to have nearly identical activation energies of <19 kcal/mol. Because of limitations in the quantum mechanical model, these numbers are likely to be somewhat high. Both reactions are slightly exothermic. Predicted barriers are similar to those of other free radicals and triplet carbenes. Our results support previous conclusions that intermediates like both 1 and 2 are involved in triplet allene photoreactions. Both saddle points are predicted to have linear C--H--C geometries; however, abstraction by cyclopropylidene is found to be quite insensitive to out-of-plane bending. This saddle point flexibility may explain the facility and remarkably *unselective* intramolecular hydrogen abstraction in reactions of cyclic allenes.

Acknowledgment. We are grateful to the National Science Foundation for support of this research.

Registry No. 1, 2143-70-6; 2, 463-49-0; CH_4, 74-82-8; hydrogen, 1333-74-0.

Supplementary Material Available: Z matrix input and cartesian coordinates for saddle points SP1 and SP2 (6 pages). Ordering information is given on any current masthead page.

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[19] (a) Rauk, A.; Drake, A. F.; Mason, Stephen F. *J. Am. Chem. Soc.* **1979**, *101*, 2284. (b) Lam, B.; Johnson, R. P. *J. Am. Chem. Soc.* **1983**, *105*, 7479.

[20] Martin, P. S.; Yates, K.; Csizmadia, I. G. THEOCHEM **1988**, *170*, 107.

Synthesis of Quinolinequinones and 1,2,3,4-Tetrahydroquinolinequinones via Cyclobutenediones

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N-Benzyl-1,2,3,4-tetrahydrocyclobuta[*b*]pyridine-5,6-dione is easily synthesized and functions as a synthetic equivalent of the unstable pyridiocyclobutenedione. Regiospecific introduction of unsaturated nucleophiles at the more reactive carbonyl group, followed by thermolysis in xylene in vessels open to air, rapidly establishes the tetrahydroquinolinequinone system which can be oxidized to the corresponding quinolinequinone with 2,3-dichloro-5,6-dicyanoquinone.

Within the last few years, cyclobutenediones (1) have emerged as versatile reagents for the construction of highly substituted quinones.[1-7] Addition of an unsaturated nucleophilic reagent to 1 followed by thermolysis leads to

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