sylate (1.12)[19] Our polarimetric value for (−)-1 is not plagued by label scrambling[20] and closely parallels the value (~1.22) usually ascribed to a "limiting" solvolysis.[1f,21]

Our optical activity results preclude symmetrical bridging as the primary basis for the exo-like rate. Nonbonded interactions and precise trajectories in U-shaped regions deserve close attention, as proposed by H. C. Brown.[22]

Acknowledgment. This research was supported by the National Science Foundation and the National Institutes of Health.

Registry No. (±)-1, 103478-21-3; (−)-1, 103478-22-4; (±)-*exo*-**5a**, 103531-56-2; (±-*endo*-**5a**, 103531-57-3; (±)-*exo*-**6a**, 103531-58-4; (±)-*endo*-**6a**, 103531-59-5; *exo*-**6b**, 61800-14-4; D_2, 7782-39-0; *endo*-2-norbornyl brosylate, 840-89-1.

Supplementary Material Available: Physical constants and spectral and analytical data for brosylates 1, *exo*-**5a**, *endo*-**5a**, *exo*-**6a**, and *endo*-**6a** (2 pages). Ordering information is given on any currrent masthead page.

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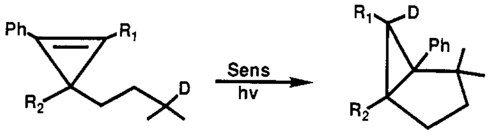
Received April 2, 1986

Deuterium Isotope Effects in the Intramolecular Hydrogen-Transfer Reactions of Some 1-Alkyl-Substituted Cyclopropenes

Summary: The photochemical behavior and deuterium isotope effect of a number of 1-alkyl-substituted cyclopropenes which contain a hydrogen atom in the γ-position of the side chain have been studied. The results are consistent with the Kwart proposal wherein nonlinear hydrogen-transfer reactions show temperature-independent isotope effects.

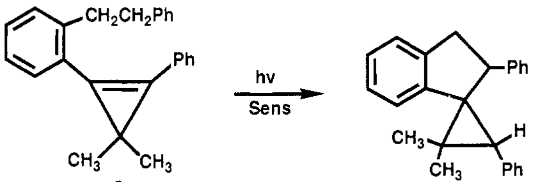
Sir: Triplet-sensitized irradiation of 3-alkyl-substituted cyclopropenes which possess γ-hydrogen leads to products involving intramolecular transfer from the side chain to the π–π* excited state of the alkene.[1-4] A mechanism involving a short-lived triplet biradical has been proposed,[2-4] having some relation to the n,π* triplet process in the type II reaction of aralkyl ketones.[5] The magnitude of the primary isotope effect in the hydrogen-transfer reaction was found to be markedly dependent on the nature of the substituent groups attached to the double bond.[4] The symmetrically substituted diaryl isomer exhibited an isotope effect significantly larger than any previously reported value for hydrogen transfer to an excited state.[6]



1; R_1=Ph; R_2=CH_3 (k_H/k_D~20/1)
2; R_1=CH_3; R_2=Ph (k_H/k_D~3.5/1)

The present contribution addresses additional details of the hydrogen-transfer reaction with structurally related cyclopropenes. The hydrogen-transfer reaction is thought to proceed by way of a nonlinear six-membered transition state.

The triplet-sensitized photobehavior of **3** in benzene (thioxanthone) produced spirobenzocyclopentane **4** in 81% isolated yield (Φ = 0.26). The structure of **4** was based on its characteristic spectral data and was further supported by a single-crystal X-ray structure analysis.[7] With carbonyl compounds, efficient intramolecular abstraction of hydrogen requires that the C–H-bond axis be directed toward the half-vacant n orbital of the carbonyl oxygen atom.[8] With alkenes, 1,5-hydrogen shifts generally take place only when γ-hydrogen atoms are absent.[9] In the above case, however, photocyclization proceeds via a seven-membered transition state. Similar behavior was encountered with cyclopropene **5**. When the sensitized irradiation of **5** was carried out in benzene (thioxanthone), spirobenzocyclopentane **6** was obtained as the exclusive photoproduct in 85% isolated yield (Φ = 0.24) [NMR ($CDCl_3$, 360 MHz) δ 0.82 (s, 3 H), 0.87 (s, 3 H), 1.57 (s, 1 H), 1.90 (br s, 1 H), 3.19 (d, 1 H, *J* = 15.0 Hz), 3.25 (d, 1 H, *J* = 15.0 Hz), 4.95 (s, 1 H), 6.95–7.35 (m, 9 H)].



3

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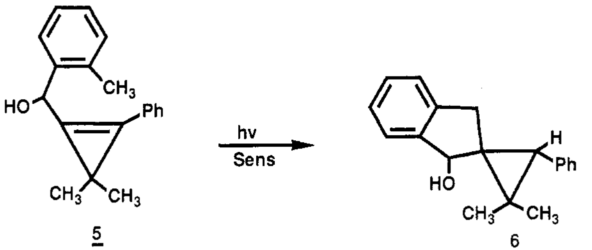

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6

We have also studied the triplet-induced photobehavior of cyclopropenes **7** and **8**. The sensitized irradition of **7** produced the 2-methylpentenyl trans-substituted cyclopropane **9** in high yield (85%, Φ = 0.21) [NMR ($CDCl_3$,

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(7) Compound 4 crystallizes in the monoclinic space group *P*21/*n* with eight molecules per unit cell. The cell constants are *a* = 14.558 Å, *b* = 8.689 Å, *c* = 29.709 Å, and *β* = 90.86°. The unit cell is nearly orthorhombic. Further details will be reported in our full paper.

(8) Turro, N. J.; Weiss, D. S. *J. Am. Chem. Soc.* **1968**, *90*, 2185.

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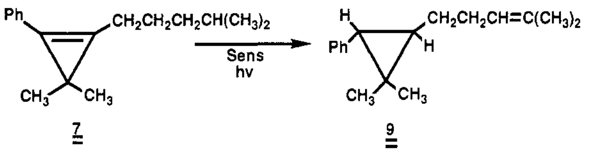
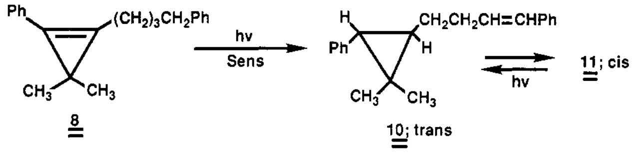
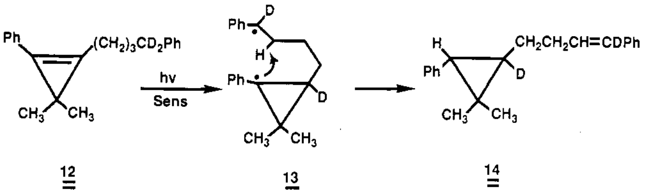




360 MHz) δ 0.90 (s, 3 H), 1.11 (q, 1 H, J = 6.5 Hz), 1.30 (s, 3 H), 1.53–1.69 (m, 2 H), 1.62 (d, 1 H, J = 6.5 Hz), 1.76 (s, 3 H), 1.80 (s, 3 H), 2.24 (q, 2 H, J = 7.3 Hz), 5.30 (t, 1 H, 7.3 Hz), 7.20–7.40 (m, 5 H)]. Similar behavior was observed with cyclopropene **8**. Consideration of the product distribution as a function of time showed that the trans isomer **10** was initially formed.[10] Isomerization about the π-bond to the cis isomer **11** occurred only when the photolysis was carried out for longer periods of time. The exclusive formation of **10** probably reflects the most stable conformation of the initially generated diradical intermediate and parallels the thermodynamic difference in olefin stability.[11]

In order to provide more detailed information concerning the hydrogen-transfer reaction, we have examined the effect of incorporating a deuterium atom onto the δ-position of the side chain. Synthesis of the desired substrate **12** involved treating 1-phenyl-2-chloro-3,3-dimethylcyclopropene[12] with lithium metal followed by reaction with 1-bromo-4,4-dideuterio-4-phenylbutane. The NMR spectrum of the resulting sensitized photoproduct **14** showed the complete absence of the quartet at δ 1.08.[10]



Thus, the reaction is completely stereospecific and involves transfer of the deuterium atom via a six-membered transition state. The high regiospecificity of hydrogen transfer is probably a consequence of the stereoelectronic requirements for abstraction as well as the fact that the resulting diradical (i.e., **13**) allows for maximum delocalization of the radical centers. Another point worth noting is that **13** prefers to undergo exclusive disproportionation rather than coupling as was encountered with cyclopropene **3**. The transition state for disproportionation requires that the C–H bond in the γ-position of the side chain be in close proximity to the radical center on the cyclopropane ring. This geometry is most easily attained with diradical **13**.

The quantum yield for the triplet-state hydrogen-transfer reaction **8** decreased substantially with deuterium substitution (Φ_8 = 0.25 vs. Φ_{12} = 0.085).[13] The value of the isotope effect (k_H/k_D ca. 3.0) for this system correlates well with related results in the literature[15] indicating an early transition state according to Hammond's postulate.[16] It is also of interest to consider the geometrical details of the transition state involving transfer of the γ-hydrogen atom to the triplet π–π^* state. Formation of an orthogonal triplet with the above systems is inconceivable as a result of structural constraints. The internal hydrogen-abstraction reaction is probably subject to the normal stereoelectronic requirement that the C–H bond being attacked (i.e., γ C–H) lie along the axis of the planar π–π^* excited state. Kwart has proposed that the geometries of transition states involving transfer of hydrogen can be analyzed by determination of the temperature dependence of the kinetic deuterium isotope effect.[17,18] The ratio of A factors should be in the range of 0.75–1.2 for a linear transition state whereas a nonlinear hydrogen transfer will be characterized by a ratio of A factors greater than 1.2. The consequence of this is that the nonlinear transfer will result in a temperature-independent isotope effect of magnitude greater than 1.2. Although this theory is relatively untested and has met controversy,[19] it was thought to have the potential of giving useful insight into the transition-state geometry of the present hydrogen-transfer reaction. Examination of Dreiding models of the molecular geometry associated with the 1,5-hydrogen-transfer reaction clearly shows the nonlinear arrangement of atoms. Determination of the isotope effect resulting from the sensitized irradiation of **8** and **12** shows the lack of a temperature dependence[20] and is therefore consistent with the Kwart proposal.

Further mechanistic details of these reactions are in progress and will be reported in due course.

Acknowledgment. We gratefully acknowledge support of this work by the National Science Foundation.

Registry No. **3**, 103836-75-5; **4**, 103836-76-6; **5**, 103836-77-7; **6**, 103851-07-6; **7**, 103836-78-8; **8**, 103836-80-2; **9**, 103836-79-9; **10**, 103836-81-3; **11**, 103836-82-4; **12**, 103851-09-8; **14**, 103836-83-5; O_2, 7782-39-0; $PCD_2(CH_2)_3Br$, 103851-08-7; 1-phenyl-2-chloro-3,3-dimethylcyclopropene, 56895-72-8.

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Received February 26, 1986

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[10] NMR **10** (360 MHz, $CDCl_3$) δ 0.80 (s, 3 H), 1.08 (q, 1 H, J = 6.8 Hz), 1.22 (s, 3 H), 1.52–1.76 (m, 3 H), 2.34–2.42 (m, 2 H), 6.29 (dt, 1 H, J = 16.0 and 6.8 Hz), 6.42 (d, 1 H, J = 16.0 Hz), 7.15–7.35 (m, 10 H).

[11] For a somewhat related example in carbonyl group photochemistry, see: Wagner, P. J.; Kelso, P. A. *Tetrahedron Lett.* **1969**, 4151.

[12] Henseling, K. O.; Weyerstahl, P. *Chem. Ber.* **1975**, *108*, 2803.

[13] The quantum yield for reaction of these unsymmetrically substituted cyclopropenes was found to depend on the concentration of starting material (0.025 M). As a consequence of this dependence, it was not possible to determine the rate of hydrogen abstraction by Cristol's method.[14]

[14] Cristol, S. J.; Micheli, R. P. *J. Am. Chem. Soc.* **1978**, *100*, 850.

[15] Bergman, N. A.; Saunders, W. H.; Melander, L. *Acta Chem. Scand.* **1972**, *26*, 1130. Pryor, W. A.; Kneipp, K. G. *J. Am. Chem. Soc.* **1971**, *93*, 5584.

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[17] Kwart, H. *Acc. Chem. Res.* **1982**, *15*, 401.

[18] We believe that the first step to produce the two benzylic radicals is rate-controlling and is therefore sensitive to isotopic substitution at the benzylic carbon. One of the reviewers has suggested that if there is an additional path where hydrogen can sometimes be transferred first to produce the less stable secondary radical followed by an internal disproportionation, then the isotope effect for this path would be close to unity. The observed isotope effect would be the weighted average of the two paths. Further discussion of this point will be dealt with in our full paper.

[19] Li, M. Y.; San Fillipo, J. *Organometallics* **1983**, *2*, 544. Hess, B. A.; Schaad, L. J. *J. Am. Chem. Soc.* **1983**, *105*, 7185. Vitale, A. A.; San Fillipo, J. *J. Am. Chem. Soc.* **1982**, *104*, 7341.

[20] The value of the isotope effect remained constant (ca. 3.0) from -20 °C to +65 °C.

[†] Alexander von Humboldt Senior Scientist, 1985; University of Wurzburg.