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KINETIC DEUTERIUM ISOTOPE EFFECTS OPERATIVE DURING TRIPLET-SENSITIZED [2+2] PHOTOCYCLIZATION OF *syn*- AND *anti*-SESQUINORBORNATRIENES

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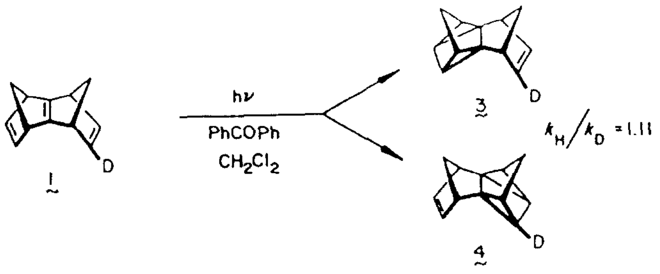
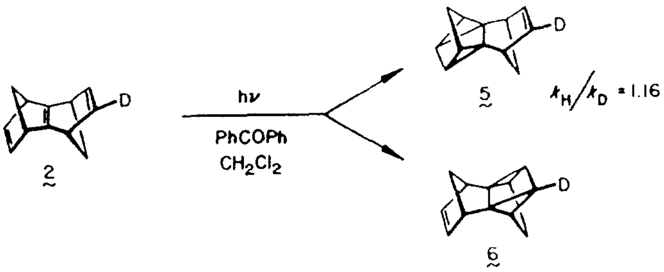
Abstract: Triplet-sensitized excitation of **1** and **2** leads under kinetic control to quadricyclanes **3-6** where the valence isomers possessing olefinic-bound deuterium dominate by a factor of 1.11-1.16.

Considerable theoretical interest[2] has recently been directed toward the contrasting pyramidalization tendencies observed crystallographically for *syn*- and *anti*-sesquinorbornene and their derivatives.[2c,3] Whereas members of the syn series give evidence of possessing a pi bond rigidly constrained in the endo direction, those sesquinorbornenes with anti stereochemistry partake most often, though not always, of planar geometry. This significantly attenuated bending is seemingly consonant with computational assessments of relative deformation energies.[2e,f] In this context, the Bartlett observation that photochemically generated *syn*-sesquinorbornene triplets undergo reduction with endo delivery of hydrogen is particularly striking.[2a] A reversed (exo) bending of the central double bond has been suggested to occur during triplet excitation.[2a,e]

With our recent acquisition of the monodeuterated trienes **1** and **2**[4] has come an interest in evaluating the kinetic isotope effects that arise during their intramolecular triplet-sensitized [2+2] cyclization to quadricyclane valence isomers. Is the D atom capable of exerting positional control (olefinic- versus cyclopropyl-bound) in the competitive ring closure? If so, to what extent? Whereas the orbital alignment in **3** and **4** appears rather ill-suited for possible photoequilibration, that present in **5** and **6** is not. Attention must accordingly also be given to determining whether the $\underline{k}_H/\underline{k}_D$ values are the end result of a kinetic or equilibrium process.

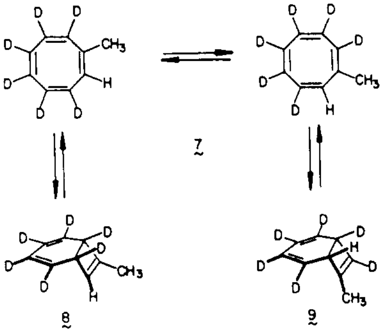




Thoroughly degassed dichloromethane solutions of 1 and 2 containing small amounts of benzophenone were sealed in NMR tubes and irradiated with a 450 W Hanovia lamp contained in a Pyrex immersion well. The intact reaction mixtures were analyzed in turn by expanded-scale proton-decoupled ^2H NMR spectroscopy as recorded by a Bruker 500-MHz instrument.[5] Integration of the signal at 6.05 ppm due to 3 revealed its area to dominate over that attributable to **4** and located at 1.20 ppm by the ratio of 1.11 (±0.05).[6] Similarly, the olefinic-bound deuterium signal for **5** at 5.63 ppm exceeded in intensity the absorption due to **6** (1.20 ppm) by the margin of 1.16 (±0.05).[6] These entirely similar k_H/k_D values indicate that deuterium is positioned preferentially at an olefinic site in the quadricyclane, irrespective of the particular structural geometry.

Evidence that the predescribed excited-state cyclizations are kinetically controlled was gained by independent preparation of pure samples of 3 and 5 and demonstration that these specifically labelled hydrocarbons fail to undergo quadricyclane-quadricyclane rearrangement, i.e., 3 $\not\rightleftharpoons$ **4** and 5 $\not\rightleftharpoons$ 6, under the present (and several other) reaction conditions. Isomers **4** and **6** are assumed to be equally incapable of triplet energy transfer and deuterium scrambling.

The present isotopic fractionation factors contrast in magnitude and direction to those observed during valence isomerization of **7** ($K_{8/9}$ = 1.08).[7] Furthermore, it has long been known that deuterium, under equilibrium conditions, prefers attachment to differently hybridized carbon atoms in the order C_{sp^3} (aliphatic) > C (cyclopropyl) > S_{sp^2} (olefinic). The higher zero point energies of C-H and C-D bond energies at cyclopropyl sites that are responsible for the ground-state imbalances can be approximated by the Bigeleisen equation or force field calculations.[8] At the experimental level, the semibullvalene **10a** $\rightleftarrows$ **11a** ($K_{25°C}$ = 1.11)[9] and barbaralone **10b** $\rightleftarrows$ **11b**[10] examples nicely illustrate these influences.[11]

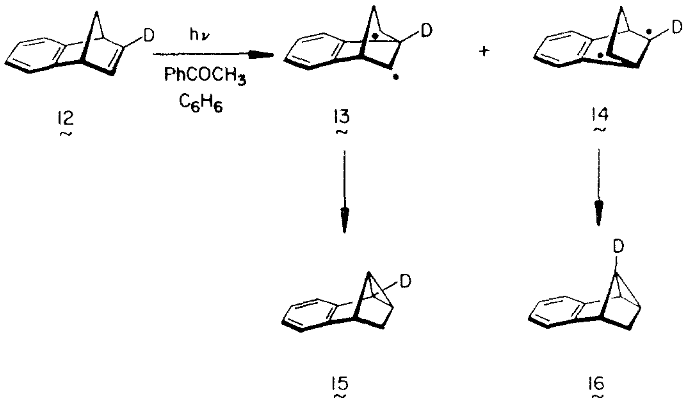


10 **11**

a, X=—; R=CH$_3$

b, X=CO; R=H

The excited triplet states of **1** and **2** clearly respond in a manner contrary to the preceding expectations. The cause of this phenomenon likely resides in the well recognized capability of deuterium to reduce rate constants for radiationless conversion to ground state.[12] Franck-Condon factors account for the major portion of this decrease because they are dependent upon overlap of the vibrational wave function for the lowest vibrational level of the initial electron state with an isoenergetic high vibrational level of the ground state and this overlap generally decreases with increasing vibrational quantum number. Since the high energy C-H stretching vibrations are dominant in acquiring the vibrational energy in the radiationless transition, cascade from the triplet hypersurfaces to the respective quadricyclane S_0 states will preferably involve the flanking olefinic bond that is undeuterated. In either case, a concerted [2+2] cycloaddition probably operates. In fact, the data suggest that the present mechanism differs fundamentally from that associated with the di-π-methane rearrangement of benzonorbornadiene-2-*d* (**12**), where the intervention of biradicals **13** and **14** (and not aryl-vinyl bridging) allows for much greater partitioning between **15** and **16** ($k_{15/16}$ = 1.37).[13]



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References and Notes

(1) Postdoctoral fellowship awardee of the Deutsche Forschungsgemeinschaft, 1985-1986.

(2) (a) Bartlett, P. D.; Roof, A. A. M.; Winter, W. J. J. Am. Chem. Soc. **1981**, 103, 6520. (b) Gleiter, R.; Spanget-Larsen, J. Tetrahedron Lett. **1982**, 927; Tetrahedron **1983**, 39, 3345. (c) Hagenbuch, J.-P.; Vogel, P.; Pinkerton, A. A.; Schwarzenbach, D. Helv. Chim. Acta **1981**, 64, 1818. (d) Jørgensen, F. S. Tetrahedron Lett. **1983**, 5289. (e) Houk, K. N.; Rondan, N. G.; Brown, F. K.; Jorgensen, W. L.; Madura, J. D.; Spellmeyer, D. C. J. Am. Chem. Soc. **1983**, 105, 5980. (f) Johnson, C. A. J. Chem. Soc., Chem. Commun. **1983**, 1135.

(3) For selected examples, see (a) Watson, W. H.; Galloy, J.; Bartlett, P. D.; Roof, A. A. M. J. Am. Chem. Soc. **1981**, 103, 2022. (b) Paquette, L. A.; Charumilind, P.; Böhm, M. C.; Gleiter, R.; Bass, L. S.; Clardy, J. Ibid. **1983**, 105, 3136. (c) Paquette, L. A.; Hayes, P. C.; Charumilind, P.; Böhm, M. C.; Gleiter, R.; Blount, J. F. Ibid. **1983**, 105, 3148. (d) Ermer, O.; Bödecker, C.-D. Helv. Chim. Acta **1983**, 66, 943. (e) Paquette, L. A.; Green, K. E.; Hsu, L.-Y. J. Org. Chem. **1984**, 49, 3650. (f) Gajhede, M.; Jørgensen, F. S.; Kopecky, K. R.; Watson, W. H.; Kashyap, R. P. J. Org. Chem. **1985**, 50, 4395.

(4) (a) syn isomer: Paquette, L. A.; Künzer, H. submitted for publication. (b) anti isomer: (E)-1,2-bis(phenylsulfonyl)ethylene-1-d was heated with tricyclo[5.2.1.0^{2,6}]deca-2,5,8-triene and the above-plane adduct [Paquette, L. A., et al., J. Am. Chem. Soc. **1986**, 108, 3453] was reductively desulfonylated.

(5) We thank Dr. Charles Cottrell of our Campus Chemical Instrumentation Center for his assistance with the recording of these spectra.

(6) The greater intensity of the vinyl deuterium absorptions is not due to fortuitous overlap with signals due to **1** and **2**, which at 6.74 and 6.75 ppm, respectively, are well separated.

(7) Paquette, L. A.; Kitching, W.; Heyd, W. E.; Meisinger, R. H. J. Am. Chem. Soc. **1974**, 96, 7371.

(8) Shiner, V. J.; Jr. In "Isotope Effects in Chemical Reactions", Collins, C. J. and Bowman, N. S., eds.: van Nostrand Rheingold, New York, 1970, Ch. 2.

(9) Askani, R.; Kalinowski, H.-O; Weuste, B. Org. Magn. Reson. **1982**, 18, 176.

(10) Barborak, J. C.; Chari, S.; Schleyer, P. v. R. J. Am. Chem. Soc. **1971**, 93, 5275.

(11) The equilibrium isotope effect for the degenerate rearrangement of the 1-(2,3-dimethylcyclopropyl)ethyl cation is also in this direction ($K_{25\,°C} = 1.11$): Siehl, H.-U.; Koch, E.-W. J. Chem. Soc., Chem. Commun. **1985**, 496.

(12) Swenton, J. S. In "Isotopes in Organic Chemistry, Volume 1", Buncel, E. and Lee, C. C. Ed., Elsevier, Amsterdam: 1975, Chapter 5.

(13) Paquette, L. A.; Varadarajan, A.; Burke, L. D. J. Am. Chem. Soc. in press.

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