Competition of a Free Rotor and a Rigid Double Bond in a Di-π-methane Rearrangement. Photolysis of a 2-Methylenebicyclo[2.2.2]octadiene

Richard T. Luibrand* and Eugene M. Fujinari

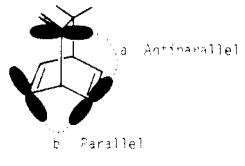
Department of Chemistry, California State University, Hayward, California 94542

Received June 11, 1979

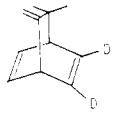
The photochemistry of 3,3-dimethyl-2-methylenebicyclo[2.2.2]octa-5,7-diene (1) has been investigated. The compound provides an opportunity for an intramolecular competition between di-π-methane photorearrangements in which an endocyclic double bond can react with either another constrained, rigid, endocyclic double bond or a free rotor methylene. A di-π-methane photorearrangement occurred despite the presence of the free rotor; the reaction is regiospecific and formed only 4,4-dimethyl-3-methylenetricyclo[3.3.0.0^{2,8}]oct-6-ene (**5**). By examining the rearrangement of deuterium-labeled material (**2**), we showed that reaction of the constrained double bonds is preferred to the reaction involving the exocyclic methylene.

The di-π-methane photorearrangement[1] is a general reaction of 1,4-dienes which has been useful in the synthesis of vinylcyclopropanes.[2] A hypothesis has been proposed for correlating the structure–multiplicity relationships observed in di-π-methane rearrangements: molecules containing only rigid, constrained, double bonds (e.g., bicyclic systems) react via the excited triplet state, while those containing nonrigid double bonds (e.g., acyclic systems) react via the excited singlet state. Nonrigid double bonds react via the excited singlet because triplet-energy dissipation by rotation of a free rotor[1,3] can provide a competing pathway. Although these generalizations correlate numerous examples of di-π-methane photochemistry, several exceptions do exist in which the presence of a free rotor in a molecule does not inhibit the triplet-state reaction.[4-6]

In an attempt to gain further insight into the effect of the presence of a free rotor in bicyclic molecules, we have investigated the photochemistry of 3,3-dimethyl-2-methylenebicyclo[2.2.2]octa-5,7-diene (1). This compound



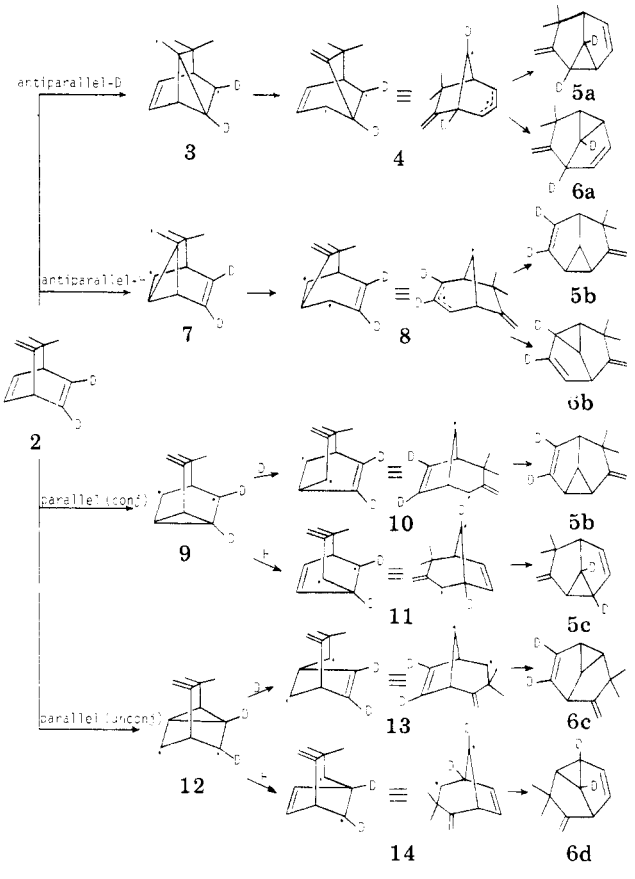
1



2

provides an opportunity for an intramolecular competition between two di-π-methane pathways. An endocyclic double bond can react with either the exocyclic methylene (antiparallel geometry (a)) or the other endocyclic double bond (parallel geometry (b)). Initial interaction of the p orbitals (**1**, a and b) should be approximately equal in both cases, so that any preference of one pathway over the other will be a reflection of either the free rotor effect or some preference of one geometrical relationship of the double bonds over the other (antiparallel and parallel). Since

Scheme I



either pathway can lead to the same product(s) a deuterium label was incorporated into the starting material **2**; this allows differentiation between the possible modes of reaction (Scheme I).

If di-π-methane rearrangement occurs involving the endocyclic and exocyclic double bonds (antiparallel, Scheme I), tricyclic products **5a**, **6a**, **5b**, and **6b** should be formed in almost equal amounts.[7] If only the endocyclic double bonds are involved (parallel), products **5b** and **5c** and/or **6c** and **6d** should be formed, depending upon the relative energies of intermediates **9** and **12**.

Results

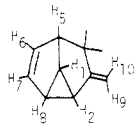
Synthesis of **2**, was carried out via a Diels–Alder reaction between 6,6-dimethylcyclohexadienone[8] and maleic an-

(1) Hixson, S. S.; Mariano, P. S.; Zimmerman, H. E. *Chem. Rev.* **1973**, *73*, 531–551.
(2) (a) Murray, R. K., Jr.; Babiak, K. A. *Tetrahedron Lett.* **1974**, 319–322. (b) Nitta, M.; Tada, M. *Chem. Lett.* **1977**, 59–62.
(3) (a) Swenton, J. S.; Crumrine, A. R.; Walker, T. J. *J. Am. Chem. Soc.* **1970**, *92*, 1406–1407. (b) Zimmerman, H. E.; Pratt, A. C. *Ibid.* **1970**, *92*, 1407–1408, 1409–1410. (c) Zimmerman, H. E.; Epling, G. A. *Ibid.* **1970**, *92*, 1411–1412.
(4) (a) Mariano, P. S.; Ko, J. K. *J. Am. Chem. Soc.* **1972**, *94*, 1766–1776. (b) Mariano, P. S.; Ko, J. K. *Ibid.* **1973**, *95*, 8670–8678.
(5) Ipaktschi, J. *Chem. Ber.* **1972**, *105*, 1840–1853.
(6) (a) Goldschmidt, Z.; Gutman, V. *Tetrahedron* **1974**, 3327–3331. (b) Goldschmidt, Z.; Worchel, A. *Tetrahedron Lett.* **1973**, 3621–3622, 3623–3624. (c) Goldschmidt, Z.; Kende, A. S. *Ibid.* **1971**, 4625–4628.
(7) Secondary kinetic isotope effects, if any, would be small.
(8) Alder, K.; Flock, F.; Lessenich, H. *Chem. Ber.* **1957**, *90*, 1709–1720.

0022-3263/80/1945-0958$01.00/0

hydride. The adduct was deuterated[9,10] and converted to **2** by electrolytic oxidation[12] and Wittig reaction.[13] The NMR spectrum of undeuterated **2** unambiguously confirms the structure. The major mass spectral fragmentation corresponds to a retro-Diels–Alder cleavage to benzene and dimethylallene.

Upon direct irradiation of **2** in hexane using a 450-W Hanovia high-pressure lamp fitted with a Vycor filter, no rearrangement was observed after 47 h. When acetone was used as a solvent and triplet sensitizer, irradiation resulted in the formation of a single rearrangement product as determined by gas–liquid chromatographic analysis using FFAP (packed and capillary) and silver nitrate–triethylene glycol columns. Preparative GLC (FFAP) provided analytically pure material corresponding to 4,4-dimethyl-3-methylenetricyclo[3.3.0.0^{2,8}]oct-6-ene[14] (**5**). The 180-MHz



5

15
λ_{max} 208 nm
(ϵ 5300)

16
λ_{max} 225–235 nm sh
(ϵ 2400)

NMR spectrum of the undeuterated photoproduct indicated a tricyclo[3.3.0.0^{2,8}]octene skeleton:[15] (C_6D_6/CCl_4) δ 0.88 (s, 3 H, CH_3), 1.17 (s, 3 H, CH_3), 1.80 (m, H_8, J_{28} = 6.5, J_{18} = 7, J_{78} = 2.24 Hz), 2.14 (t, 1 H, H_2, J_{28} = 6.5, J_{12} = 6.6, J_{29} = 0.9, J_{210} = 1.1 Hz), 2.39 (q, 1 H, H_1, J_{12} = 6.6, J_{15} = 5.72, J_{18} = 7 Hz), 2.59 (d of d, 1 H, H_5, J_{15} = 5.72, J_{56} = 2.36 Hz), 4.85 (t, 1 H, H_{10}, J_{210} = 1.1, J_{910} = 0.9 Hz), 5.07 (s, 1 H, H_9), 5.43 (m, 1 H, H_6, J_{67} = 5.51, J_{56} = 2.36 Hz), 5.64 (d of d, 1 H, H_7, J_{67} = 5.51, J_{78} = 2.24 Hz). Particularly characteristic of this system is the H_1 absorption which appears as a quartet.[16] The couplings were verified by spin-decoupling experiments which also indicated long-range coupling between H_1 and H_6 (previously reported in **15** by Chapman[16a]), H_8 and H_6, H_2 and H_6, and H_5 and H_9 (small). The allylic coupling of H_2 with both H_9 and H_{10} unambiguously defines the structure as assigned in **10**. This is confirmed by comparison of the UV spectrum (λ_{max} 225 nm sh (ϵ 5700)) with model compounds **15**[16a] and **16**.[17]

The formation of deuterated photoproduct **5** from the antiparallel mechanism (Scheme I) would result in the formation of almost equal amounts of **5a** and **5b**.[7] Similarly, reaction of the parallel double bonds (Scheme I) must result in almost equal amounts of **5b** and **5c**.[7] The calculated average protium distribution for the two mechanisms is listed in Table I.

Table I. Hydrogen Atom Distribution for 5, Product of Photolysis of 2

signal position, δ	assignment	hydrogen atom distribution: calcd[a] for antiparallel av[b]	calcd[a] for parallel av[c]	found[d]
1.80	H_8	1.00	0.53	0.555
2.14	H_2	0.53	1.00	0.876
2.39	H_1	0.53	0.53	0.551
2.59	H_5	1.00	1.00	0.908
5.43	H_6	0.53	0.53	0.653
5.64	H_7	0.53	0.53	0.558

[a] Normalized to 4.10 protons, based on residual protium as determined by falling-drop deuterium analysis.[10] [b] Values obtained by averaging the results expected from equal formation of **5a** and **5b** (Scheme I). [c] Values obtained by averaging the results expected from equal formation of **5b** and **5c** (Scheme I). [d] Determined by integration of the ^{1}H NMR signals (180 MHz FT NMR), normalized to 4.10 protons.[10]

Discussion

A concerted variation of the antiparallel pathway could result in products **5a** and **5b** (but not **6a** and **6b**). Similarly, concerted variations of the parallel pathways could result in products **5b** and **5c** and/or **6c** and **6d**.

A comparison of the experimental hydrogen distribution of product **5** with the calculated values (Table I) clearly shows that products **5b** and **5c** were formed in the photolysis of **2**; products **5a** and **5b** were not. Thus the parallel pathway is preferred over the antiparallel one depicted in Scheme I. In deciding whether the parallel mechanism leading to **5** is concerted or not, one can argue by analogy to a related reaction. The elegant and extensive work by Zimmerman and co-workers[18] on the conversion of barrelene to semibullvalene suggests that a concerted mechanism is unlikely in both cases.

The formation of **5**, but not **6**, in the photolysis of **2** (Scheme I) provides another example of a regiospecific di-π-methane reaction.[19] This can be explained by the stabilization of diradicals **9**–**11** by conjugative interaction with the cyclopropyl ring and the exocyclic methylene. Such stabilization is not present in diradicals **12**–**14**, making the first pathway the preferred.[20]

The occurrence of di-π-methane rearrangement of **2** is contrary to the result predicted by the free rotor hypothesis,[1,3] since reaction occurs despite the presence of an exocyclic methylene which could dissipate triplet energy by rotation.[5,6] The free-rotor hypothesis, however, can be used to rationalize the preference for reaction via the endocyclic double bonds (parallel pathway) in **2**. Initial bonding between the endocyclic double bonds results in formation of diradical **9** (Scheme I) which has no opportunity for triplet-energy dissipation via the exocyclic methylene. If, on the other hand, the exocyclic methylene participates in initial bonding forming diradicals **3** or **7** (Scheme I, antiparallel pathway), triplet energy can be dissipated by rotation of the methylene, resulting in a return to ground state starting material. The free-rotor hypothesis thus provides an explanation for the results that we have observed. Alternative explanations could be that **9** is more stable than **3** or **7** (Scheme I), i.e., that the cis

(9) Atkinson, J. G.; Csakuary, J. J.; Herbert, G. T.; Stuart, R. S. *J. Am. Chem. Soc.* **1968**, *90*, 498–499.
(10) Deuterium incorporation was determined to be 95% of two hydrogens.[11]
(11) Falling-drop deuterium analysis was carried out by Josef Nemeth, Urbana, IL.
(12) (a) Radlick, P.; Klem, R.; Spurlock, S.; Sims, J. J.; van Tamelen, E. E.; Whitesides, T. *Tetrahedron Lett.* **1968**, 5117–5121. (b) Westberg, H. H.; Dauben, J., Jr. *Ibid.* **1968**, 5123–5126.
(13) Monson, R. S. "Advanced Organic Synthesis: Methods and Techniques"; Academic Press: New York, 1971; pp 105–106.
(14) Bryce-Smith, D.; Foulger, B. E.; Gilbert, A. *J. Chem. Soc., Chem. Commun.* **1972**, 664–665.
(15) We are grateful to Rudy Nunlist and the University of California, Berkeley, NMR laboratory for these spectra.
(16) (a) Chapman, O. L.; Borden, G. W.; King, R. W.; Winkler, B. *J. Am. Chem. Soc.* **1964**, *86*, 2660–2663. (b) Wilzbach, K. E.; Kaplan, L. *Ibid.* **1966**, *88*, 2066–2067. (c) Zimmerman, H. E.; Givens, R. S.; Pagni, R. M. *Ibid.* **1968**, *90*, 6096–6108.
(17) Zimmerman, H. E.; Bailey, R. W.; Givens, R. S.; Grunewald, G. L.; Sherwin, M. A. *Ibid.* **1969**, *91*, 3316–3323.
(18) Zimmerman, H. E.; Boettcher, R. J.; Buehler, N. E.; Keck, G. E.; Steinmetz, M. G. *J. Am. Chem. Soc.* **1976**, *98*, 7680–7689 and references therein.
(19) Hart, H.; Love, G. M. *J. Am. Chem. Soc.* **1973**, *95*, 4592–4599.
(20) Paquette, L. A.; Meisinger, R. H. *Tetrahedron Lett.* **1970**, 1479–1482.

configuration of the cyclopropyldicarbinyl radical is more stable than the trans, or that there is a preference for di-π-methane reaction involving double bonds in the parallel geometry over the antiparallel.[21]

Experimental Section

Elemental and mass spectral analyses were performed by University of California Analytical Services and Mass Spectroscopy Laboratories, Berkeley, CA. Electron-impact mass spectra were recorded on a Nova 3 data general computer in line with a Finnigan/INCOS 2300 data system and AEI MS-12 mass spectrometer. Infrared spectra were obtained on a Perkin-Elmer Model 337 grating spectrometer. NMR spectra (60 MHz) were recorded on a JEOL C60 HL spectrometer. The 180-MHz NMR spectra were obtained by the courtesy of the University of California.[15] UV spectra were recorded on a Varian Series 634 spectrometer. Melting points were obtained using a capillary and are uncorrected.

3,3-Dimethylbicyclo[2.2.2]octa-5,7-dien-2-one. The Diels–Alder adduct of 6,6-dimethylcyclohexadienone and maleic anhydride (11.2 g, 0.51 mol) was dissolved in a solution of triethylamine (7.4 mL) and water (92 mL) and was added to an electrolysis cell[12] containing 680 mL of pyridine. A 100-V dc potential was applied to the stirred solution resulting in an initial current of 0.8 A. The temperature was maintained at 20–24 °C and electrolysis was discontinued when the current dropped to 0.1 A. The resulting black solution was diluted with water (900 mL) and extracted with pentane (continuous). The pentane extract was washed successively with 2 N hydrochloric acid (pH of washings, 1), saturated sodium hydrogen carbonate (5 × 250 mL), and saturated sodium chloride solution. The pentane solution was dried (Na_2SO_4) and concentrated (Vigreux column), resulting in 4.3 g (57%) of crude 3,3-dimethylbicyclo[2.2.2]-octa-5,7-dien-2-one (yellow-orange solid). Purification was carried out by preparative VPC (4% FFAP on 60/80 Chrom G, 0.25 in. × 10 ft, 110 °C, He flow 60 mL/min), resulting in 3,3-dimethylbicyclo[2.2.2]octa-5,7-dien-2-one as white crystals: mp 108–109 °C; retention time 40 min; IR ($CHCl_3$) 2975 (m), 1718 (s), 1470 (m), 1385 (m), 1365 (w), 1348 (m), 1064 (m); NMR (CCl_4) δ 1.1 (s, 6 H, methyl), 3.8 (m, 1 H, bridgehead), 4.3 (m, 1 H, bridgehead), 6.7 (m, 4 H, vinyl). Anal. Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 80.96; H, 8.15.

3,3-Dimethyl-2-methylenebicyclo[2.2.2]octa-5,7-diene (2h). Sodium hydride (50% mineral oil dispersion, 0.96 g) was purified in a flame-dried three-necked round-bottom flask by stirring with petroleum ether (3 × 50 mL) and decanting the solvent, followed by evacuation and nitrogen flushing. Dimethyl sulfoxide (distilled from calcium hydride, 12 mL, 0.169 mol) was added, and the solution was heated at 70–75 °C with stirring until the evolution of hydrogen ceased. This solution was cooled in an ice bath and methyltriphenylphosphonium bromide (7.10 g, 0.018 mol) dissolved in 20 mL of dimethyl sulfoxide was immediately added and stirred at room temperature for 10 min. 3,3-Dimethylbicyclo[2.2.2]octa-5,7-dien-2-one (0.73 g, 0.005 mol) was added and the solution stirred for 30 min at room temperature. Vacuum distillation (Vigreux column, 55 torr, oil bath, 100 °C) resulted in sublimation of white crystals which were dissolved in 30 mL of petroleum ether and washed with water (5 × 10 mL). Analytically pure 3,3-dimethyl-2-methylenebicyclo[2.2.2]octa-5,7-diene (**2h**) (0.813 g, 25%) was obtained by preparative VPC (FFAP, same conditions as above, retention time 6.8 min): mp 84–85 °C; IR (n-C_6H_{14}) 3050 (m), 1645 (m), 1150 (w), 930 (w), 818 (w), 878 (s), 741 (s), 686 (w), 664 (m), 604 (w) cm^{-1}; NMR ($CDCl_3$) δ 1.12 (s, 6 H, methyl), 3.28–3.67 (m, 1 H, bridgehead), 3.67–4.33 (m, 1 H, bridgehead), 4.75 (s, 1 H, methylene), 5.05 (s, 1 H, methylene), 6.64 (m, 4 H); mass spectrum, m/e (%) 39 (30), 40 (15), 41 (19), 51 (20), 52 (11), 53 (37), 66 (12), 67 (68), 68 (100), 77 (17), 78 (28), 91 (20), 131 (31), 146 (14); UV (n-C_6H_{14}) strong end absorption at 200 nm. Anal. Calcd for $C_{11}H_{14}$: C, 90.33; H, 9.67. Found: C, 90.49; H, 9.60.

Photorearrangement of 3,3-Dimethyl-2-methylenebicyclo[2.2.2]octa-5,7-diene (2). A solution of 0.1833 g (0.0013 mol) of 2-methylene-3,3-dimethylbicyclo[2.2.2]octa-5,7-diene in 10 mL of acetone (degassed by bubbling nitrogen through the solution for 1 h) in a quartz tube was irradiated for 20 h at room temperature with a 450-W Hanovia high-pressure lamp fitted with a Vycor filter and a water-cooled quartz immersion well.

The sample was concentrated (20-cm Vigreux column) and purified by preparative VPC (4% FFAP on 60/80 Chrom G, 0.375 in. × 20 ft, 138 °C, He flow 120 mL/min). The starting material (22.3 mg, 12%) eluted in the first fraction (retention time 27.0 min). The second fraction (retention time 30.2 min) yielded 61.2 mg (33%) of 4,4-dimethyl-3-methylenetricyclo[3.3.0.$0^{2,8}$]oct-6-ene (**5**) as a colorless oil: IR (n-C_6H_{14}) 3040 (m), 2815 (m), 1655 (m), 1635 (m), 1360 (s), 1350 (m), 923 (m), 911 (m), 894 (m), 878 (s), 800 (m), 765 (s), 752 (s), 736 (s), 725 (m) cm^{-1}; NMR (see text); mass spectrum, m/e (%) 39 (31), 41 (17), 51 (17), 53 (19), 65 (12), 67 (10), 77 (19), 78 (19), 91 (47), 103 (10), 115 (18), 116 (21), 129 (12), 131 (100), 132 (10), 146 (26); UV (n-C_6H_{14}) λ_{max} 225 sh nm (ϵ 5700). Anal. Calcd for $C_{11}H_{14}$: C, 90.33; H, 967. Found: C, 90.25; H, 9.64.

Deuterium Incorporation. A mixture of 10 g (45.4 mmol) of 6,6-dimethylcyclohexadienone–maleic anhydride adduct,[8] 30 mL of deuterium oxide (99.5 mol%), and 6.25 mmol of sodium deuterioxide (prepared from 0.1 mL of deuterium oxide and sodium metal) was placed in a stainless steel bomb calorimeter and heated at 150 °C for 24 h.[9] After cooling, the bomb was opened and 5 mL of 5% hydrochloric acid was added with stirring, resulting in rapid crystallization. The product was filtered, washed with water, and dried. This process was repeated four additional times to yield 7.65 g (70%) of dicarboxylic acid as off-white crystals: mp 208–210 °C; mass spectrum, M^+ 240 indicated the incorporation of two deuterium atoms; NMR (CD_3OD) δ 1.03 (s, 3 H, methyl), 1.12 (s, 3 H, methyl), 3.00–3.44 (m, 2 H, bridgehead), 6.00–6.50 (m, 2 H, vinyl).

5,6-Dideuterio-3,3-dimethyl-2-methylenebicyclo[2.2.2]-octa-5,7-diene (2). The dicarboxylic acid obtained upon deuteration of the 6,6-dimethylcyclohexadiene–maleic anhydride adduct was converted to **2** using the electrolysis and Wittig conditions given for the undeuterated compounds. Falling-drop deuterium analysis indicated 95% deuterium incorporation of two hydrogen atoms. NMR [(CCl_4) δ 1.11 (s, 6 H, methyl), 3.33 (m, 1 H, bridgehead), 3.98 (m, 1 H, bridgehead), 4.56 (s, 1 H, methylene), 4.86 (s, 1 H, methylene), and 6.40 (m, 2 H, vinyl)] confirmed that the deuterium atoms were on the endocyclic double bonds.

Registry No. **2**, 55693-16-8; **2**-d_2, 72610-16-3; **5**, 72610-17-4; 3,3-dimethylbicyclo[2.2.2]octa-5,7-dien-2-one, 55693-20-4; 6,6-dimethylcyclohexadienone, 21428-63-7; maleic anhydride, 108-31-6; 2,3-dideuterio-7,7-dimethyl-8-oxobicyclo[2.2.2]oct-5-en-2,3-dicarboxylic acid, 72610-18-5; sodium deuterioxide, 14014-06-3.

(21) Support for this work by a Cottrel Research Grant from the Research Corporation is gratefully acknowledged.