the PDIGM type[21,22] was used (written in BASIC for an Apple Macintosh PC).

Acknowledgment. We thank the National Science Foundation (CHE-8009670) and the Hochschuljubiläumsstiftung der Stadt Wien for financial support and Dr. H. Kalchhauser for experimental help.

Registry No. 1, 833-48-7; 1m, 75969-44-7; 2, 1210-34-0; 2m, 114818-63-2; 3, 1210-35-1; 3m, 86324-68-7.

Supplementary Material Available: Experimental details on crystallography, empirical force-field calculations, the Cambridge Data Base search, and the lanthanide induced shift experiments, the final atomic coordinates and isotropic thermal parameters (Table VI), and the proton coordinates (Table VII) (8 pages). Ordering information is given on any current masthead page.

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[40] Armitage, I.; Dunsmore, G.; Hall, L. D.; Marshall, A. G. *Can. J. Chem.* 1972, *50*, 2119.

Response of Tricyclo[5.5.0.0^{2,8}]dodecatetraene, Tricyclo[5.3.0.0^{2,8}]deca-3,5,9-triene, and 9,10-Dimethylenetricyclo[5.3.0.0^{2,8}]deca-3,5-diene to Thermal and Photochemical Activation

Jürgen Dressel,[1] Paul D. Pansegrau, and Leo A. Paquette*

Evans Chemical Laboratories, The Ohio State University, Columbus, Ohio 43210

Received March 23, 1988

The light-sensitive tetraene 1 is relatively stable at room temperature in diluted form. Dimerization/polymerization does, however, occur slowly when 1 is stored in neat condition. At temperatures in the vicinity of 100 °C, 1 rearranges smoothly to Kukla's hydrocarbon (7) by a concerted [1,3] carbon migration. Irradiation with long wavelength light (366 nm) also leads to 7 and, to a lesser extent, bicyclo[6.4.0]pentaene (12). In contrast, 2 rearranges at 20 °C and below via isobullvalene (14) to lumibullvalene (15). Appropriate deuterium labeling has shown this rearrangement to proceed via biradical 18. When heated to 80 °C in benzene, 3 undergoes smooth first-order isomerization to 22 with a half-life of 65 min. The underlying causes of this divergent behavior are discussed in terms of orbital symmetry allowedness.

As in spiroconjugated systems, the level and consequences of through-bond interaction between two π-ribbons linked orthogonally across a cyclobutane ring is intimately related to the total number of electrons involved.[2] Whereas the split between the first two photoelectron (PE) bands of **1**[3,4] amounts to 1.44 eV and points to a strong through-bond interaction between the cyclobutane relay and the peripheral π-systems,[5] the PE spectra recorded for **2**[4,6] reveal a lack of interaction between its two olefinic fragments. The PE spectrum of **3**[4,7] has an appearance similar to that of 1.


1


2


3

Herein, we report on the varied responses of **1–3** to heat and light. Tricyclo[3.3.0.0^{2,6}]octa-3,7-diene (**4**), the smallest member of this series earlier synthesized by Meinwald[8a] and by Zimmerman,[9a] exhibits in its UV spectrum a bathochromic shift to 300 nm (contrast the λ_{max} for **6** at 250 nm)[8b] that has invited theoretical analysis.[2,10] The notable thermal lability of **4** (estimated $t_{1/2}$ of 10 min at room temperature)[9b] and its ready isomerization to semibullvalene (**5**) have precluded PE analysis.


4 5


6

Thermal and Photochemical Rearrangement of 1. During monitoring of the formation of **1** by analytical gas chromatography (GC), two peaks were noted in the (CH)$_{12}$ range, their ratio being markedly dependent on the injection port temperature. Under controlled conditions (C_6D_6, 102 °C, sealed NMR tube), **1** isomerized cleanly and quantitatively to **7**[11] ($k = 1.8 \times 10^{-4}$ s^{-1}; $t_{1/2} = 63$ min). Homonuclear proton decoupling permitted specific assignment to be made to the ^{1}H NMR signals of **7** (see Experimental Section). Many similarities were seen between **7** and bicyclo[3.2.1]octa-2,6-diene, previously analyzed by Brown and Occolowitz.[12]

The stage was now set for use of deuterium labeling as a probe of mechanistic detail. Halogen–lithium exchange in the 3,9-dibromo derivative[4] followed by a D_2O quench gave **1**-d_2 with 87% deuterium incorporation. The D_{2d} symmetry of **1** causes C-3, -6, -9, and -12 to be equivalent. Consequently, **1**-d_2 can be considered to be quadruply labeled as shown in **8**. When **1**-d_2 in carbon tetrachloride solution was thermolyzed for 5 h at 110–115 °C in a sealed

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[1] Fulbright Scholar, 1982–1983; Evans Fellow, 1985–1986.

[2] (a) Bischof, P.; Gleiter, R.; Haider, R. *Angew. Chem., Int. Ed. Engl.* 1977, *16*, 110; (b) *J. Am. Chem. Soc.* 1978, *100*, 1036.

[3] Paquette, L. A.; Dressel, J.; Chasey, K. L. *J. Am. Chem. Soc.* 1986, *108*, 512.

[4] Dressel, J.; Chasey, K. L.; Paquette, L. A. *J. Am. Chem. Soc.*, in press.

[5] Gleiter, R.; Toyota, A.; Bischof, P.; Krennrich, G.; Dressel, J.; Pansegrau, P. D.; Paquette, L. A. *J. Am. Chem. Soc.*, in press.

[6] Dressel, J.; Paquette, L. A. *J. Am. Chem. Soc.* 1987, *109*, 2857.

[7] Paquette, L. A.; Dressel, J.; Pansegrau, P. D. *Tetrahedron Lett.* 1987, *28*, 4965.

[8] (a) Meinwald, J.; Tsuruta, H. *J. Am. Chem. Soc.* 1969, *91*, 5877; (b) 1970, *92*, 2579.

[9] (a) Zimmerman, H. E.; Robbins, J. D.; Schantl, J. *J. Am. Chem. Soc.* 1969, *91*, 5878. (b) Frey, H. M.; Hopkins, R. G. *J. Chem. Soc. B* 1970, 1410.

[10] (a) Gleiter, R.; Kobayashi, T. *Helv. Chim. Acta* 1971, *54*, 1081. (b) Kanda, K.; Koremoto, T.; Imamura, A. *Tetrahedron* 1986, *42*, 4169.

[11] (a) Paquette, L. A.; Kukla, M. J.; Ley, S. V.; Traynor, S. G. *J. Am. Chem. Soc.* 1977, *99*, 4756. (b) Kukla, M. J. Ph.D. Thesis, The Ohio State University, Columbus, OH, 1974.

[12] Brown, J. M.; Occolowitz, J. L. *J. Chem. Soc. B* 1968, 411.

0022-3263/88/1953-3996$01.50/0

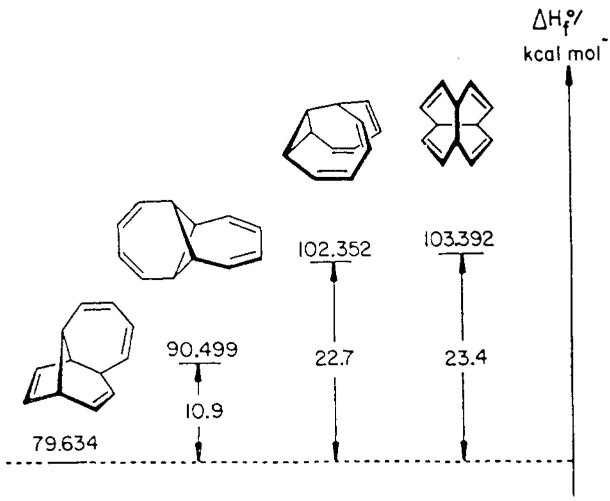
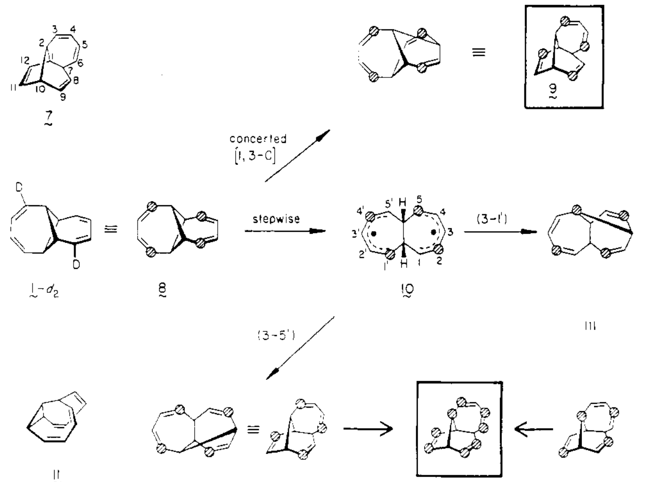


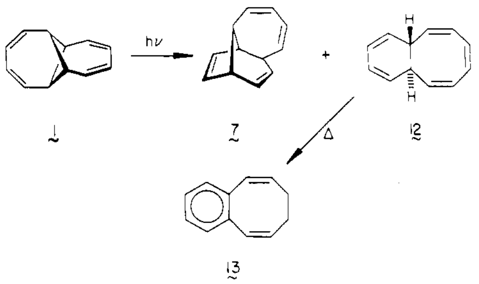
Figure 1. Heats of formation of select $(CH)_{12}$ valence isomers (MMP2).

NMR tube, only 4 of the 12 possible positions in **9** showed deuterium incorporation, all with approximately the same intensity (^2H NMR analysis at 77 MHz). Since ^2H and ^1H chemical shifts show close correspondence, the deuteriated sites in **9** were easily identified. Any possible secondary kinetic isotope effects reside within the error limits of detection and were therefore not considered.



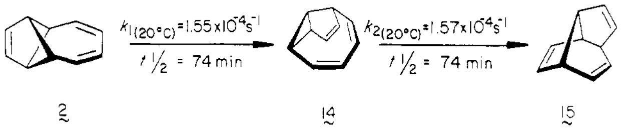
Of the various mechanistic alternatives available to **1**, only a formally concerted [1,3] carbon migration[13] is consistent with these findings. Full symmetrization via **10**, which would have distributed the isotopic label over eight sites, clearly was not realized. Also, any passage through isomer **11** can be discounted as well, since the heat of formation of this semibullvalene-like structure (102.35 kcal mol^{-1}) reveals it to be of considerably higher energy than **1** (90.50 kcal mol^{-1}, see Figure 1) and consequently not likely attainable by thermal activation of this magnitude (see Figure 1).[2b,14]

When irradiated at 366 nm, **1** again gave rise to **7**. Under these circumstances, a minor product tentatively identified as *trans*-bicyclo[6.4.0]dodeca-2,4,6,9,11-pentaene (**12**)[19] was also formed. Identification of **12** is predicated on its spectral characteristics[20] and the readiness with which it isomerizes to **13**[21] during attempted GC purification. Exposure of **1** [λ_{max} 218 (ϵ 8900)] to shorter wavelength (254 nm) provided **7**, **12**, and some benzene, the ultimate thermodynamic sink of benzene dimers.



When 1-d_2 was irradiated in CH_2Cl_2 at 366 nm, **9** was again the only tricyclo[5.5.0.0^{2,10}]dodecatetraene formed. In **12**-d_2, the isotopic label was scrambled over all positions, with the heaviest deuterium concentration at δ 5.56. Thus, **1** finds [1,3] sigmatropic migration to be most accessible from its ground and excited states.

Thermal Isomerization of 2. When solutions of **2** in $CDCl_3$ were allowed to warm to 20 °C and monitored at frequent time intervals by 300-MHz spectroscopy, isomerization to isobullvalene (**14**) was observed to occur relatively rapidly. Structural assignment to **14** was deduced by comparison with chemical shift data reported earlier by Masamune[22] and by Katz.[23] After a short induction period, signals attributable to lumibullvalene (**15**)[24,25] developed and finally replaced completely those due to **14**. The relevant first-order kinetic data are incorporated alongside the formulas.[26] Although the C_2 symmetry axis in **15** reduces the number of ^{13}C signals to only five, the ^1H NMR spectrum is not similarly simplified because of the existence of long-range spin–spin interactions of significant magnitude. Isotopic labeling studies to be de-



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[13] Berson, J. A. *Acc. Chem. Res.* **1972**, *5*, 406.

[14] Obviously, the heats of formation of the different $(CH)_{12}$ valence isomers have to be treated with some measure of caution, since the force-field calculations do not encompass electronic interactions. As an example, the through-bond interaction in **1** is predicted to be destabilizing by MINDO/3.[2b,15] The puckering angle of 28.5° for cyclobutane as determined by Allinger's MM2 force-field program[16] is close to the experimental value of 35°,[17] although the energy barrier to ring inversion is somewhat underestimated (0.9 kcal mol^{-1} instead of 1.5 kcal mol^{-1}).[17,18]

[15] Bingham, R. C.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 1285, 1294.

[16] Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127.

[17] Miller, F. A.; Capwell, R. J. *Spectrochim. Acta* **1971**, *27A*, 947.

[18] Stone, J. M. R.; Mills, I. M. *Mol. Phys.* **1970**, *18*, 631.

[19] (a) Rottele, H.; Martin, W.; Oth, J. F. M.; Schröder, G. *Chem. Ber.* **1969**, *102*, 3985. (b) Oth, J. F. M.; Rottele, H.; Schröder, G. *Tetrahedron Lett.* **1970**, 61.

[20] The ^1H NMR spectrum of the second rearrangement product fits both **12** and its cis-fused epimer. However, the latter is known to undergo a rapid hexatriene-cyclohexadiene electrocyclic ring closure at 20 °C followed by fragmentation to benzene.

[21] (a) Wittig, G.; Eggers, H.; Duffner, P. *Liebigs Ann. Chem.* **1958**, *619*, 10. (b) Buchanan, G. W.; McCarville, D. R. *Can. J. Chem.* **1973**, *51*, 177. (c) Meier, H.; Molz, T.; Merkle, U.; Echter, T.; Larch, M. *Liebigs Ann. Chem.* **1982**, 914. (d) Farnum, D. G.; Ghandi, M.; Raghu, S.; Reitz, T. *J. Org. Chem.* **1982**, *47*, 2598.

[22] Hojo, K.; Seidner, R. T.; Masamune, S. *J. Am. Chem. Soc.* **1970**, *92*, 6641.

[23] (a) Katz, T. J.; Cheung, J. J.; Acton, N. *J. Am. Chem. Soc.* **1970**, *92*, 6643. (b) Katz, T. J.; Cheung, J. J. *Ibid.* **1969**, *91*, 7772.

[24] Jones, M., Jr. *J. Am. Chem. Soc.* **1967**, *89*, 4236.

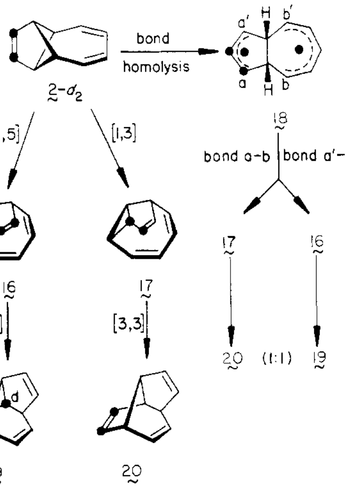
[25] (a) Paquette, L. A.; Kukla, M. J. *J. Am. Chem. Soc.* **1972**, *94*, 6874. (b) Kukla, M. J. Ph.D. Thesis, The Ohio State University, Columbus, OH, 1974.

[26] Following completion of this study, a report appeared describing an inability to isolate **2** in favor of **29**: (a) Gleiter, R.; Zimmermann, H.; Sander, W. *Angew. Chem.* **1986**, *98*, 893]. (b) Gleiter, R.; Zimmermann, H.; Sander, W.; Hauck, M. *J. Org. Chem.* **1987**, *52*, 2644.

scribed below necessitated that all proton shifts within **15** be accurately defined.[27]

The thermal isomerization of **2** to **14** can occur by three different mechanisms: (1) a concerted, thermally allowed [1,5] carbon shift across the diene bridge (**2** → **16**); (2) a concerted, thermally forbidden [1,3] carbon shift across the ethylene bridge (**2** → **17**);[29] and (3) a stepwise diradical process involving homolysis of any of the four symmetry-equivalent cyclobutane σ bonds (**2** → **18**).[30] Suitable isotopic labeling of **2** can differentiate between these hypothetical pathways, particularly since the conversion of **14** to **15** has previously been demonstrated to be the exclusive result of pure [3,3] sigmatropy.[23b] Thus, reliable accounting can be made of the fate of the individual carbons in the second stage of the isomerization, i.e., **16** → **19** and **17** → **20**.

Since α-chloro sulfones[31] and even episulfones[32] are capable of hydrogen–deuterium exchange prior to sulfur extrusion, it proved an easy matter to prepare **2**-d_2 by exposure of its α-chloro sulfone precursor[3] to an excess of potassium *tert*-butoxide in cold (−70 °C) to tetrahydrofuran containing deuterium oxide and gradual warming of this mixture to 0 °C. A total of 0.46 D was incorporated into the ethylenic bridge of **2**. Although the triene was not likely equivalently deuteriated at both sites, this issue is unimportant since the C_{2v} symmetry of **2** does not allow independent distinction of these positions.



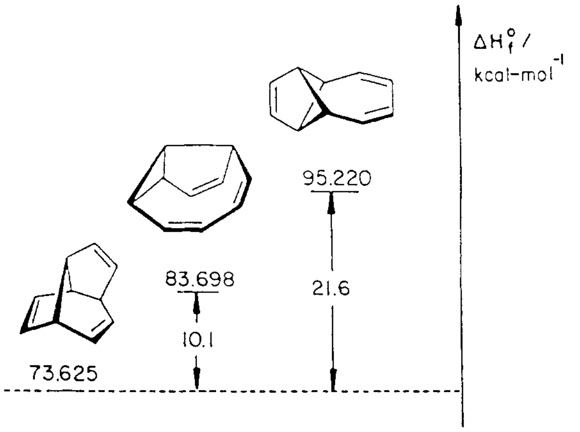


Figure 2. Heats of formation of select $(CH)_{10}$ valence isomers (MMP2).

The labeling patterns within lumibullvalene expected from the three candidate processes are (1) H_c:H_d, 1:1; (2) H_a:H_c, 1:1; (3) H_a:H_c:H_d, 1:2:1. Any possible secondary isotope effects were expected to be on the order of 10% or less. When the rearrangement of **2**-d_2 in carbon tetrachloride solution at 20 °C was monitored by ^2H NMR spectroscopy at 77 MHz, three absorptions appeared at δ 6.63, 5.57, and 3.13 with an intensity ratio of 1.0:2.1:1.0.

Although this ratio can be rationalized in terms of competing concerted [1,3] and [1,5] shifts which happen to have the same rate constants, this possibility is considered to be highly unlikely because the thermally allowed concerted pathway should have a more favorable energy of activation than the thermally forbidden one.[26b] On the other hand, formation of diradical **18** is fully compatible with our observations. Since this intermediate possesses a mirror plane, identical (save for the isotope effects) ring closure rate constants (k_{ab} and $k_{a'b'}$) explain the equal proportion of **19** and **20**. Importantly, the possibility that **16** and **17** might otherwise symmetrize via forbidden [3,5] sigmatropic rearrangement has been ruled out.[23b]

Thermal Rearrangement of 3. When **3** was heated to 80 °C in benzene solution, smooth first-order rearrangement occurred ($t_{1/2}$ = 65 min). GC-MS analysis of the reaction mixture showed the tetraene to be 92% converted into an isomer of m/z 156 during this period. Suitable C–H correlation and COSY studies at 500 MHz identified the product to be **22**. Key spectral features supportive of the isobullvalene assignment are the lone doubly allylic proton at δ 3.42–3.39 and the three cyclopropyl resonances at δ 1.81–1.78, 1.56–1.53, and 1.36–1.32. These shifts compare favorably with those recorded for isobullvalene (**14**) which are located at δ 2.00–1.93, 1.80–1.72, and 1.57–1.48.

The formation of **22** can result from direct concerted [1,5] sigmatropic rearrangement or via a diradical process mediated by **21**.

Comparative Analysis of the Responses of Relay-Conjugated Perpendicular π Systems to Thermal Activation. Within the series of tricyclic hydrocarbons that have the latent potential for interaction of two mutually perpendicular π-ribbons through a cyclobutane ring, thermal lability is seen to decrease dramatically from tricyclo[3.3.0.0^{2,6}]octa-3,7-diene (**4**) through **2** and **3** to tricyclo[5.5.0.0^{2,8}]dodecatetraene (**1**), an order that conforms nicely with the progressive reduction in ring strain. As in the case of tetraene **1**, MMP2 force-field calculations

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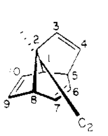
[27] By deuterium labeling Katz and Cheung established that the rearrangement of **14** to **15**



15

is a concerted Cope rearrangement and thereby identified the signal at δ 2.46 as position (8 and 5).[23b] Therefore the remaining aliphatic proton at δ 3.17 must correspond to position 2 (and 1). The coupling constant of J = 5.6 Hz between the signals at δ 6.69 and δ 5.60, a value typical for vicinal, vinylic protons, suggests that they belong to positions 9 and 10 (3 and 4). Consequently, the remaining vinylic proton at δ 5.92 should be position 7 (and 6). This also explains the dramatic simplification of this signal on irradiation at δ 2.46, since both form an AA′XX′ spin subsystem. In both bicyclo[3.2.1]octa-2,6-diene[12] and tricyclo[5.5.0.0^{2,10}]dodeca-3,5,8,11-tetraene,[3,28] position 5 absorbs downfield from position 6. In analogy, the signal at δ 6.69 would correspond to position 9 (and 3), the signal at δ 5.60 to position 10 (and 4).

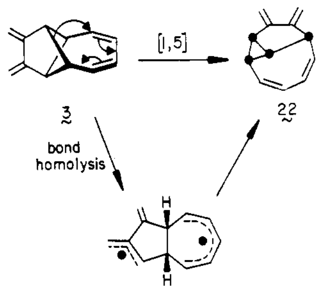
[28] Dressel, J. Ph.D. Thesis, The Ohio State University, Columbus OH, 1987, p 84.

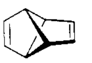
[29] Berson, J. A. *Acc. Chem. Res.* **1972**, *5*, 406.

[30] Diradical **18** is recognized to be involved in the high-temperature degenerate thermal rearrangement of lumibullvalene.[25]

[31] See, for example: (a) Paquette, L. A. *J. Am. Chem. Soc.* **1964**, *86*, 4085. (b) Paquette, L. A.; Philips, J. C.; Wingard, R. E., Jr. *Ibid.* **1971**, *93*, 4516.

[32] (a) Neureiter, N. P.; Bordwell, F. G. *J. Am. Chem. Soc.* **1963**, *85*, 1209. (b) Neureiter, N. P. *Ibid.* **1966**, *88*, 558.





4

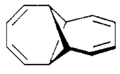
$t_{1/2}$ (20 °C) = 10 min[9]

2

$t_{1/2}$ (20 °C) = 74 min

3

$t_{1/2}$ (80 °C) = 65 min



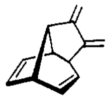
1

$t_{1/2}$ (102 °C) = 63 min

provide heat of formation data (Figure 2) that are in good agreement with the experimental observations. However, an important alteration in the energetic ordering of the various structural types takes place in going from the C_{12} series to the C_{10} class of hydrocarbons.

In the methine dodecamers, the semibullvalene-like isomer is approximately 12 kcal mol^{-1} *less thermodynamically stable* than **1** and is not accessible by heating of this particular relay conjugated system. By contrast, the $(CH)_{10}$ hypersurface is so constructed that the **2** → **14** conversion is now favored by an approximately equivalent energy gap. Associated with the subsequent [3,3] sigmatropic shift that leads from **14** to **15** is another 10 kcal mol^{-1} energy benefit. In view of the cascade available to **2**, one might well ask why the biradical derived from **2**, viz. **18**, does not immediately collapse to the ultimate energy sink **15**. The answer may lie in the principle of least motion;[33] the termini of the allyl and pentadienyl radicals lie in much closer proximity making bond formation at these positions kinetically favorable.

The thermal alternatives available to **3** are no more restricted. The structural features of biradical **21** are such that intramolecular covalent bonding can materialize to give either **22** or **23**. As with **2**, the formation of **22** is favored thermodynamically, MNDO indicating the heats of formation to differ by approximately 16 kcal mol^{-1}. The conversion to **23**, while also exothermic (by ca. 14 kcal mol^{-1}), is not observed experimentally.



23

The general trend is, therefore, characteristically one where the divinylcyclopropane isomer is formed initially, except in the case of **1**, where the strain energy of this product type is higher than that of the starting cyclobutane. Insufficient data are available to define whether **3** undergoes its structural change by concerted [1,5]sigmatropy or via a biradical intermediate. Tricyclo[$5.3.0.0^{2,8}$]deca-3,5,9-triene (**2**) follows the latter mechanistic option. For unique and incompletely understood reasons, **1** undergoes its bond reorganization by way of a seemingly concerted [1,3] carbon shift. The underlying cause of this particular phenomenon is deserving of further study.

Experimental Section

Thermal Rearrangement of 1 to Tricyclo[$5.5.0.0^{2,10}$]dodeca-3,5,8,11-tetraene (7). A. In Chloroform-*d*. Tetraene **1**[4] (2 mg, 0.01 mmol) in 0.5 mL of chloroform-*d* was sealed in an NMR tube, completely submersed in an oil bath, and kept at 80 C. The progress of the rearrangement was followed by ^{1}H NMR. Tetraene **1** rearranged with a half-life of 7 h.

For **7**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.40 (dd, $J_{11,12} = 5.7$ Hz, $J_{11,10} = 2.9$ Hz, 1, H_{11}), 6.08 (ddd, $J_{12,11} = 5.7$ Hz, $J_{12,1} = 3.0$ H, $J_{12,9} = 1.0$ Hz, 1, H_{12}), 6.04–5.87 (series of m, 5 $H_{3-6,9}$), 4.94 (dddd, $J_{8,9} = 9.4$ Hz, $J_{8,7} = 3.5$ Hz, $J_{8,1} = 1.8$ Hz, $J_{8,10} = 0.7$ Hz, 1, H_8), 2.91–2.83 (m, 1, H_7), 2.83–2.79 (m, 1, H_2), 2.77–2.72 (m, 1, H_{10}), 2.45–2.41 (m, 1, H_1) (assigned by homodecoupling); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 141.05, 134.58, 132.99, 132.08, 129.34, 127.08, 125.27, 122.36, 50.46, 44.21, 41.59, 38.25.

B. In Benzene-d_6. Tetraene **1** (7 mg, 0.05 mmol) was dissolved in 1 mL of benzene-d_6 inside a 5-mm medium-walled NMR tube. After 5 freeze pump–thaw–cycles (liquid nitrogen, 0.05 mmHg), the tube was sealed, wrapped in aluminum foil, completely submersed in an oil bath, and heated at 102 °C. The progress of reaction was followed by 300-MHz ^{1}H NMR integration.

3,9-Dideuteriotricyclo[$5.5.0.0^{2,8}$]dodeca-3,5,9,11-tetraene (1-d_2). All manipulations were performed with protection from light. Crude 3,9-dibromide[4] (30 mg, max 0.096 mmol) was dissolved in anhydrous tetrahydrofuran (3 mL) under argon. At −78 °C, *tert*-butyllithium (1.5 M in pentane, 0.67 mL, 1.0 mmol) was injected dropwise. After 5 min, the dark red solution was quenched with 99.8% deuterium oxide (0.15 mL, 7.5 mmol) at −78 °C, warmed to room temperature, and partitioned between pentane (10 mL) and water (10 mL). The aqueous phase was extracted with pentane (5 mL) and the combined organic phases were washed with water (2 × 5 mL) and brine (5 mL), dried, filtered, and evaporated. Condensation into a V-tube (dry ice/2-propanol trap, 0.05 mmHg, gentle warming with heat gun) afforded 4 mg (27%) of a white solid that melted slightly below room temperature. This material was about 73% pure by GC and ca. 87% deuteriated in positions 3 and 9. It was used as such: ^{1}H NMR (300 MHz, CCl_4, C_6D_6 insert as lock) δ 6.05–5.95 (m, 2.26, $H_{3,6}$), 5.80–5.72 (m, 4, $H_{4,5}$), 2.65–2.58 (m, 4, $H_{1,2}$); ^{2}H NMR (77 MHz, CCl_4, reference $CDCl_3$) δ 6.00; MS, m/z (M^+) calcd 158.1060, obsd 158.1062.

Thermal Rearrangement of 1-d_2. Tetraene **1**-d_2 (4 mg, 0.03 mmol) was dissolved in carbon tetrachloride (0.5 mL, spectrophotometric grade) and sealed into an NMR tube after 4 freeze–pump–thaw cycles. Completely protected from light by aluminum foil, the solution was thermolyzed in an oil bath at 110–115 °C for 5 h. For **9**: ^{2}H NMR (77 MHz, CCl_4, $CDCl_3$ as reference, relative intensities) δ 6.06 (1.00), 5.97 (1.24), 5.91 (1.11), 5.86 (1.30).

Photoisomerization of 1. A. NMR Experiment in Methylene Chloride-d_2 at 366 nm. A solution of **1** (ca. 4 mg, 0.03 mmol) in methylene chloride-d_2 (1 mL) was sealed into an NMR tube after 4 freeze–pump–thaw cycles. No rearrangement occurred within 10 min, when the sample was irradiated through an uranium glass filter with a TLC hand lamp (8-W mercury vapor, long wave range: transmission maximum 366 nm). Without being filtered, **1** rearranged completely within 51 min according to ^{1}H NMR analysis at 300 MHz. In addition to **7** (65%), **12** (35%) was tentatively identified as the second product. For **7**: ^{1}H NMR (300 MHz, CD_2Cl_2) δ 6.39 (dd, J = 5.6, 2.9 Hz, 1 H), 6.06 (dd, J = 5.9, 3.0 Hz, 1 H), 6.00–5.87 (series of m, 5 H), 4.91–4.85 (m, 1 H), 2.88–2.82 (m, 1 H), 2.82–2.69 (m, 1 H), 2.43–2.36 (br s, 1 H).

For **12**: ^{1}H NMR (300 MHz, CD_2Cl_2) δ hidden under 6.00–5.87 envelope of **7** (4 H), 5.87–5.83 (m, 2 H), 5.83–5.78 (m, 2 H), 5.55–5.48 (m, 2 H), 3.53–3.49 (m, 2 H).

B. Preparative Scale Irradiation of 1 in Pentane at 366 nm. A pentane (10 mL) solution of **1** (11 mg, 0.071 mmol) in a Pyrex test tube was carefully evacuated and flushed with argon.

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After irradiation (2 h) with a long wavelength hand TLC lamp (366 nm transmission maximum), evaporation (room temperature, 100 mmHg) and preparative GC (5 m × 4 mm 10% SE 30 Chromosorb P, 60 mL He/min, injection port: 250 °C, column: 190 °C, detector: 220 °C) yielded three components: 2.4 mg (22%) of **7** (t_R 9–11 min); 2.7 mg (25%) of a mixture (t_R 11–13 min); 1.8 mg (17%) of **13** (79% pure, t_R = 13–15 min) as colorless oils with strong musty odors. For **13**: ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.23–7.16 (m, 2 H), 7.16–7.09 (m, 2 H), 6.54 (d, J = 11.9 Hz, 2 H), 6.00–5.90 (m, 2 H), 2.33 ('t', J = 2.8 Hz, 4 H). This spectrum compares well with that described in ref 21.

C. NMR Scale Irradiation of 1-d_2 in Methylene Chloride at 366 nm. A solution of **1**-d_2 (5 mg, 0.03 mmol; 87% deuteriated in positions 3 and 9) in methylene chloride (spectrophotometric grade) was prepared as in **A** and irradiated at 366 nm for 54 min. According to ^{2}H NMR, all of the starting material was replaced by **9** and **12**-d_2. For **9**: ^{2}H NMR (77 MHz, CH_2Cl_2, reference CD_2Cl_2) δ 6.11, 6.03, 5.98, 5.93. For **12**-d_2: ^{2}H NMR (77 MHz, CH_2Cl_2) δ 5.83 (1.7), 5.75 (1.6), 5.56 (3.3), 3.50 (1.0).

Thermal Rearrangement of 2. An NMR tube containing a cold (−78 °C) solution of **2** in chloroform-*d* was equilibrated in a 300-MHz NMR spectrometer at 293 K for 10 min. Spectra were subsequently collected at 10-min intervals (eight scans took 37 s) and always integrated by using the same amplitude. The following absorptions were chosen for integration. **2**: δ 6.27–6.16 (4 H); **14**: δ 5.33 (1 H); **15**: δ 6.67 (2 H). The sum of the integrals of each scan was normalized to 100. The rate constant $k = 1.55 \times 10^{-4}$ s^{-1} corresponds to a half-life of 74 min at 20 °C.

Thermal Rearrangement of 2-d_2. A solution of the dibromo chlorosulfone precursor[3] (93 mg, 0.24 mmol) and 99.8% deuterium oxide (2.9 μL, 2.9 mmol) in anhydrous tetrahydrofuran (1.5 mL) was cooled to −70 °C, treated with 1.6 M potassium *tert*-butoxide in tetrahydrofuran (3.6 mL, 5.8 mmol), and slowly warmed to 0 °C within 1 h. After another hour at 0 °C, the reaction mixture was worked up with water and pentane at 0 °C as described above.

According to 300-MHz ^{1}H NMR ($CDCl_3$, 263 K), the hydrocarbon mixture consisted of triene **2**, the tricyclo[5.3.0.0^{2,8}]deca-4,9-diene contaminant, and isobullvalene (**14**) in a ratio of 53:43:4 with a deuterium incorporation of about 30% in the 9- and 10-positions of the diene and triene. Careful evaporation of the $CDCl_3$ and condensation mg (19%) of material that was dissolved in carbon tetrachloride and heated until all was converted into lumibullvalene-d_2 (**15**-d_2). ^{2}H NMR analysis in CCl_4 with δ ($CDCl_3$) 7.26 ppm as standard revealed the presence of three deuterium signals at 3.13, 5.57 and 6.63 ppm in a ratio of 1:2:1.

Thermal Rearrangement of 3. An NMR tube containing 15 mg of **3** in 1 mL of C_6D_6 was warmed in an 80 °C oil bath for 3.5 h. In order to obtain kinetic data, the olefinic singlets were integrated at various times. Computational and graphical determinations yielded half-lives of 68 and 63 min, respectively.

For **22**: ^{1}H NMR (500 MHz, C_6D_6) δ 6.17 (dd, J = 8.9, 11.2 Hz, 1 H), 6.03 (dd, J = 3.8, 11.2 Hz, 1 H), 5.74–5.66 (m, 2 H), 5.37 (s, 1 H), 5.32 (d, J = 3.2 Hz, 1 H), 4.93 (s, 1 H), 4.79 (d, J = 2.6 Hz, 1 H), 3.42–3.39 (m, 1 H), 1.80 (dd, J = 6.3, 12.6 Hz, 1 H), 1.55 (dd, J = 5.9, 9.4 Hz, 1 H), 1.36–1.32 (m, 1 H); ^{13}C NMR (125 MHz, C_6D_6) ppm 152.13, 149.32, 137.90, 133.96, 120.10, 127.54, 105.25, 103.10, 44.45, 27.47, 25.19, 22.09; MS, m/z (M^+) calcd 156.0917, obsd 156.0939.

Acknowledgment. The financial support of the National Science Foundation is acknowledged with gratitude. We also thank Dr. C. E. Cottrell (Campus Chemical Instrumentation Center) for the ^{2}H NMR, COSY, and C–H correlation measurements and Drs. W. Randolph Winchester and Marc-Andre Poupart for calculations.

Chemical and Physical Properties of Anthronylidene

Kurt W. Field*,[1] and Gary B. Schuster[2]

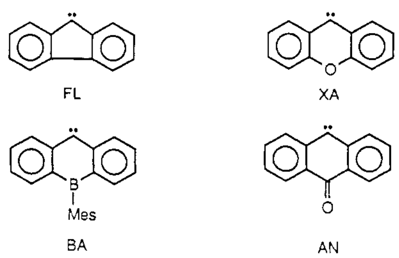
Departments of Chemistry, Bradley University, Peoria, Illinois 61625, and Roger Adams Laboratory, University of Illinois, Urbana, Illinois 61801

Received October 28, 1987

Irradiation of diazoanthrone (DAAN) leads to loss of nitrogen and to formation of the carbene anthronylidene (AN). The triplet ground state of this carbene was detected at low temperature by ESR and optical spectrometric methods and at room temperature in fluid solution by laser flash photolysis. The rate constants for the reaction of ^{3}AN with olefins, saturated hydrocarbons, and alcohols were determined spectrometrically. Combination of these kinetic measurements with the results of chemical competition studies permits estimation of the energy gap separating the ground triplet state from the lowest singlet state of AN (ΔG_{ST}) to be 5.8 ± 0.6 kcal/mol. This value is compared with that for other related carbenes and with the estimate obtained from MINDO/3 calculations for AN.

The chemical and physical properties of carbenes are remarkably sensitive to electronic perturbation. This is primarily a result of the relatively small energy difference between the highest occupied and lowest unoccupied molecular orbitals for these species.[3] Small changes in the energies of these orbitals can invert the state spin multiplicities from their usual order of triplet below singlet. It has been understood for some time on a theoretical level that there are two distinct ways to affect the energies of these orbitals.[4] The first is through a change in geometry, primarily the bond angle at the carbene carbon atom. Calculations predict that as this angle contracts, the energy of the singlet carbene decreases relative to that of the triplet. The second variable that controls the singlet–triplet gap is related to electronic perturbation.[5] This is clearly revealed experimentally in the comparison of

Chart I



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