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Valence Isomerization Equilibria of Highly Fluorinated Cycloocta-1,3,5-trienes

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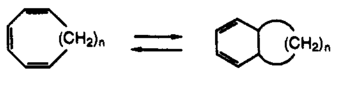
Abstract: Three interconverting 1,2,3,4,5,6-hexafluorocycloocta-1,3,5-triene/bicyclo[4.2.0]octa-2,4-diene systems have been synthesized (unsubstituted (**2**), *cis*-difluoro-substituted (**3**), and fully fluorinated (**4**) at the methylene carbons). Equilibrium constants, plus enthalpy and entropy changes for **2** and **3**, have been measured for these valence isomerizations. For cyclization of **4** the equilibrium constant is about 4300 times that of **2**. In the case of **3**, the triene exists as a rapidly interconverting 1:1 mixture of the two tub conformers, while the bicyclic isomer exists solely in the *endo*-F configuration at ordinary temperatures. Rate constants for tub–tub and triene–diene interconversion have been determined for **3**. The equilibrium constant for cyclization of octafluorocyclooctatetraene (**14**) to its bicyclic isomer is also reported, and comparisons are drawn between various quantities measured in this work and their counterparts in hydrocarbon systems. Implications of some of our findings for the strain energy content of octafluorocyclobutane are discussed.

We are engaged in an effort to learn more about the consequences of wholesale substitution by fluorine into hydrocarbon molecules. Valence isomerization equilibria can provide a sensitive measure of fluorine substituent effects. The valence isomerizations that will be examined in this paper are thermal hexatriene–cyclohexadiene interconversions. These are orbital topology-allowed, six-electron, disrotatory electrocyclic processes.[1]

In the case of hexatriene itself, the electrocyclic equilibrium lies far on the side of cyclohexadiene because of the much greater strength of a C–C σ bond relative to the corresponding π bond. Incorporation of the triene system into a ring, however, makes it possible to control the position of equilibrium. If the ends of the triene are linked by a methylene chain, as in eq 1, the electrocyclization equilibrium lies far to the left for a single methylene because of the ring strain in norcaradiene but far to the right for three or more methylenes.[2] In the special case of two methylenes, where the triene ring is eight-membered, the equilibrium constant is not far from unity. Cope was the first to observe the cycloocta-1,3,5-triene (**1t**)–bicyclo[4.2.0]octa-2,4-diene (**1d**) equilibrium,[3] and Huisgen measured the kinetic and thermodynamic parameters for the system (Table I).[4] With its balanced equilibrium, this valence isomerization is particularly well suited for a study of fluorine substituent effects.



(1)

$n = 1$ $K_{eq} \ll 1$

$n \geq 3$ $K_{eq} \gg 1$

$n = 2$ $K_{eq} \sim 1$

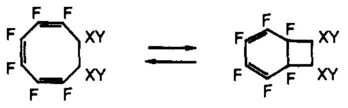
1t 1d

Here we describe the synthesis and a study of the electrocyclic equilibria of three cyclooctatriene–bicyclooctadiene systems that are fluorinated on the six carbons involved in the isomerization. The two saturated carbons are unsubstituted (**2**), *cis*-difluoro-substituted (**3**), and fully fluorinated (**4**), respectively. The letter "**t**" or "**d**" following the number of a compound identifies it as the triene or diene isomer, respectively.

Table I. Thermodynamic Data for Cyclooctatriene–Bicyclooctadiene Equilibria

system	K_{eq}(100 °C)	$\Delta G°$ (100 °C)	$\Delta H°$, kcal/mol	$\Delta S°$, eu
1t ⇌ **1d**[a]	0.14	1.5	1.1	−1
2t ⇌ **2d**[b]	0.043 ± 0.002	2.33	1.9 ± 0.4	−1 ± 1
3t ⇌ **3d**[b]	1.23 ± 0.02	−0.15	−0.8 ± 0.2	−1.8 ± 0.6
4t ⇌ **4d**[c]	180 ± 5	−3.9		

[a] Reference 15. [b] Measured in *o*-dichlorobenzene/dodecane-d_{26}, 4:1. [c] Neat liquid.



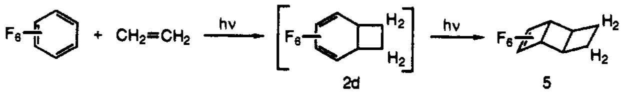
2t, 2d X = Y = H

3t, 3d X = H, Y = F (cis)

4t, 4d X = Y = F

Results and Discussion

Synthetic Methods. Ethylene adds smoothly to hexafluorobenzene under the influence of ultraviolet light.[5,6] The initially formed [2 + 2] adduct **2d** photocyclizes under the reaction conditions, yielding the volatile, crystalline tricyclooctene **5**. Its completely fluorinated analogue **6** can be prepared by the same method, but much less efficiently. Irradiation of a solution in 1,2-dichlorotetrafluoroethane (F-114) of tetrafluoroethylene and hexafluorobenzene sealed in a quartz ampule produces much polytetrafluoroethylene, even in the presence of a radical chain inhibitor, in addition to the desired adduct. Thus, a less direct but more practical synthesis of this compound was devised.



2d 5

Photocycloaddition of 1,2-dichlorodifluoroethylene to hexafluorobenzene yields a stereoisomeric mixture of *anti*-dichloroperfluorotricyclooctenes (**7**).[6] Direct fluorination of the double bond of **7** with a fluorine/helium mixture in 1,1,2-trichlorotrifluoroethane (F-113) gave a decafluoro dichloride, which yielded the desired fluoroolefin **6** upon treatment with zinc dust and

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(1) Marvell, E. N. *Thermal Electrocyclic Reactions*; Academic Press: New York, 1980; pp 260–305.

(2) Gajewski, J. J. *Hydrocarbon Thermal Isomerizations*; Academic Press: New York, 1981.

(3) Cope, A. C.; Haven, A. C.; Ramp, F. L.; Trumbull, E. R. *J. Am. Chem. Soc.* **1952**, *74*, 4867.

(4) Huisgen, R.; Mietzsch, F.; Boche, G.; Seidl, H. Organic Reaction Mechanisms. *Spec. Publ. Chem. Soc.* [*London*] **1965**, *19*, 3.

(5) For related reactions see: Zupan, M.; Sket, B. *Isr. J. Chem.* **1978**, *17*, 92–9.

(6) Lemal, D. M.; Buzby, J. M.; Barefoot, A. C., III; Grayston, M. W.; Laganis, E. D. *J. Org. Chem.* **1980**, *45*, 3118.

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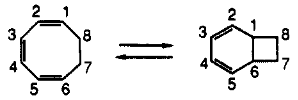
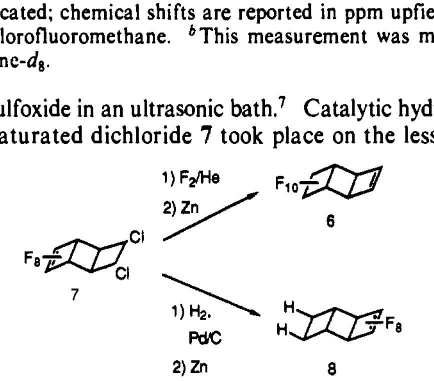
Table II. ^{19}F NMR Assignments for Cyclooctatrienes and Bicyclooctadienes[a]

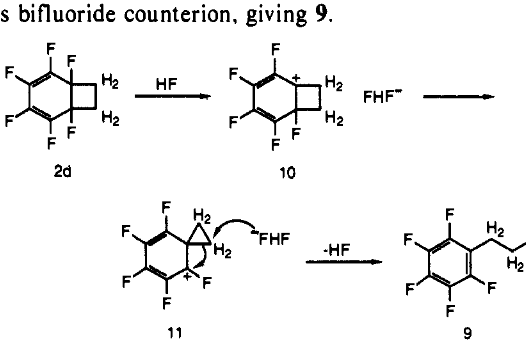


compd	F_3, F_4	F_2, F_5	F_1, F_6	F_7, F_8
2t	134.9	145.2	113.8	
3t	131.3	139.9	127.1	199.1
3t[b]	130.0	138.7	127.8	198.9
	130.7	143.6	128.4	201.6
2d	157.4	156.1	167.3	
3d	151.7	155.4	172.1	209.4
4d	147.4	154.8	188.4	123.6
				125.9

[a] Spectra were measured in chloroform-*d* at room temperature, except as indicated; chemical shifts are reported in ppm upfield from internal trichlorofluoromethane. [b] This measurement was made at −75 °C in toluene-d_8.

dimethyl sulfoxide in an ultrasonic bath.[7] Catalytic hydrogenation of the unsaturated dichloride **7** took place on the less hindered exo face of the double bond, and vicinal dechlorination as described produced dihydrofluorocarbon **8**. Tricyclic olefins **5**, **6**, and **8** all underwent smooth ring opening in silated Pyrex ampules at about 160 °C, yielding equilibrium mixtures of diene and triene (**2**–**4**). These orbital topology disallowed cyclobutene ring openings were presumably facilitated by the simultaneous release of strain in two four-membered rings.[6,7] In the case of **5**, it was found necessary to carry out the pyrolysis in the presence of calcium carbonate as an acid scavenger. If this precaution were omitted, only 2-fluoroethylpentafluorobenzene (**9**) was obtained. Probably a trace of hydrogen fluoride promoted ionization of bridgehead fluorine in **2d**; the resulting conjugated cyclobutyl cation **10** ring contracted to a spiro cation (**11**), which was vulnerable to attack by its bifluoride counterion, giving **9**.





Characterization of the Valence Isomerization Equilibria. The ^{19}F NMR spectrum of the equilibrium mixture of **2t** and **2d** comprised two sets of equal-area signals, an intense set and a far weaker set at higher field (Table II). The latter set was attributed to the bicyclic isomer **2d** by analogy to an array of model compounds,[8] which also made possible assignment of the individual signals. Bridgehead fluorines are clearly responsible for the highest field signals, and the remaining two close-lying resonances were assigned by noting that the 157.4-ppm one was much narrower than that at 156.1 ppm. In a 1,2,3,4,5,6-hexafluorobicyclo[4.2.0]octadiene F_3 and F_4 may appear either at higher or lower field than F_2 and F_5, but F_3 and F_4 characteristically display smaller spin–spin splitting than the other pair. With assignments in hand for the bicyclic form, the spectrum of the monocyclic isomer could be assigned unambiguously with the help of spin-saturation transfer measurements.[9] At 150 °C the rate of isomer interconversion was fast enough that successive irradiation of each of the three signals at low field caused a dramatic decrease in intensity of the signal at high field corresponding to the same pair of fluorines.

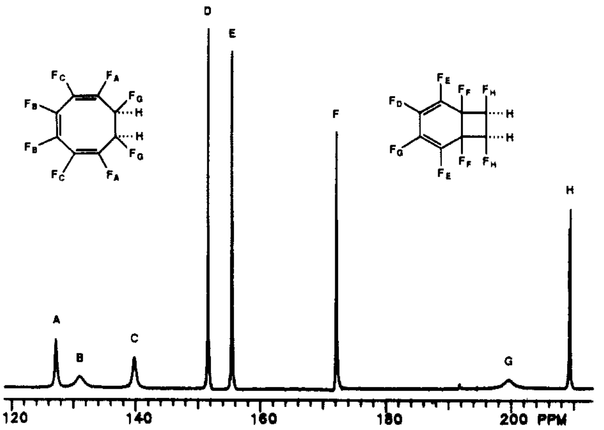


Figure 1. The 282-MHz ^{19}F NMR spectrum of equilibrating isomers **3t** and **3d** at 23 °C in chloroform-*d*. Chemical shifts are recorded in Table I.

In Table I is recorded the equilibrium constant at 100 °C for cyclization of **2t** to **2d** together with the accompanying enthalpy and entropy changes. These values were obtained by NMR integration over a range of temperatures. Cyclization is less favorable in this case than in the parent hydrocarbon system,[3] giving 4% versus 12% of the bicyclic isomer at 100 °C. In contrast, the equilibrium in the fully fluorinated system ($\mathbf{4t} \rightleftharpoons \mathbf{4d}$) lies so far to the right that the monocyclic form has not been detected by NMR spectroscopy. By capillary gas chromatography, however, it has been possible to find the minor isomer. Pure samples were equilibrated at various temperatures and then quickly quenched. GC analysis under constant, nonequilibrating conditions revealed the presence of a small peak at slightly longer retention time than the bicyclic isomer. The reversible increase in relative intensity of the small signal as a function of temperature confirmed that it represents the valence isomer and not simply a trace impurity. At 100 °C there is just 0.53% of triene in the equilibrium mixture (Table I). Thus, replacement of hydrogen by fluorine on the two saturated carbons increases the equilibrium constant at this temperature by a factor of about 4300. The ^{19}F NMR spectrum of **4d** comprises an apparent AB quartet ($J_{app} = 225$ Hz) corresponding to the two pairs of geminal fluorines and three higher field signals characteristic of the cyclohexadiene moiety, assigned as shown in Table II.

In the octafluorodihydro system ($\mathbf{3t} \rightleftharpoons \mathbf{3d}$), the 282-MHz ^{19}F NMR spectrum at room temperature comprises a set of four broad, equal-area signals and a set of four relatively sharp resonances of equal area (Figure 1). The spectrum was assigned by the methods used for **2** and **4** (see also Table II). In principle, exo and endo forms exist for both monocyclic and bicyclic forms, but only one stereoisomer of each is *apparent* in the room temperature spectrum. The sharp signals correspond to the **3d** and the broad to **3t**. In this system K_{eq} for cyclization at 100 °C is 1.23 ± 0.02, which is not far from the geometric mean, 2.8, of the equilibrium constants for the tetrahydro and fully fluorinated systems **2** and **4**. The small enthalpy and entropy changes accompanying cyclization are also shown in Table I.

The configuration of the bicyclic form **3d** was determined through nuclear Overhauser enhancement experiments.[10] When

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[7] Waldron, R. F.; Barefoot, A. C., III; Lemal, D. M. *J. Am. Chem. Soc.* **1984**, *106*, 8301.

[8] More than a dozen 1,2,3,4,5,6-hexafluorobicyclo[4.2.0]octa-2,4-dienes have been synthesized in our laboratory.

[9] Sandstrom, J. *Dynamic NMR Spectroscopy*; Academic Press: London, 1982; pp 53–8.

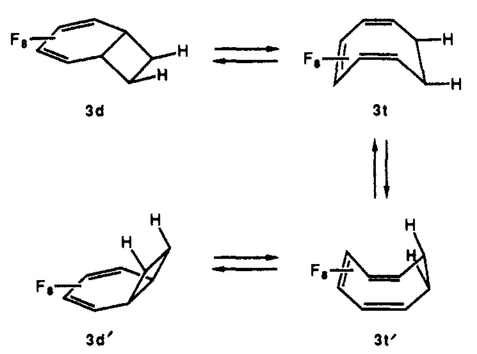

Figure 2. Interconversion pathway for endo and exo configurations of **3d** via the tub conformers of **3t**.

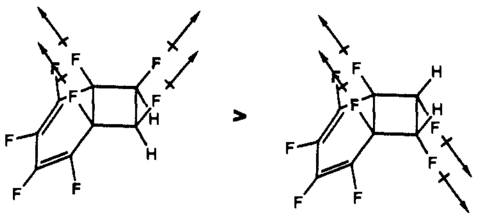

Figure 3. A comparison of repulsions between bond dipoles in the endo and exo configurations of **3d**. The negative ends of the C–F dipoles shown are much closer together in the *exo*-F form than in the endo.

the highest field signal was irradiated (fluorines geminal to hydrogen), no change was observed in the intensity of the bridgehead fluorine resonance. An intensity enhancement of about 15% was found, however, when the protons were irradiated. Thus, the hydrogens are exo in **3d**. Because exo–endo equilibration in **3d** occurs via electrocyclic ring opening to **3t** and tub inversion of the latter (Figure 2), the stereoisomer we observe is clearly the product of thermodynamic control. This finding can be rationalized in terms of repulsion between pairs of C–F bond dipoles, for the repulsion should be much larger in the stereoisomer with exo fluorines than in that with endo (Figure 3).[11]

The great breadth of the signals for **3t** in Figure 1 suggested the possibility of a rate process in the intermediate exchange rate region. If the two tub-flip conformers of this molecule existed in rapid enough equilibrium at room temperature to approach the fast-exchange limit in the 282-MHz spectrum, one would expect to see four broad signals as observed. In confirmation of this surmise, when the spectrometer was cooled down each of the four signals split into two of essentially equal area that sharpened at low temperatures. At −75 °C the equilibrium constant for interconversion of the tub-flip conformers is 1.0 (3). The rate constant for this process at −13.(8) °C (T_c for the highest field signal pair) is 1690 ± 80 s^{-1}, corresponding to a free energy of activation of 11.3 kcal/mol in toluene-d_8. For the parent hydrocarbon, 1,3,5-cyclooctatriene, St. Jacques and Prud'homme[12] found a tub-flip free energy barrier of only 6.2 ± 0.5 kcal/mol at −145 °C. The 5 kcal/mol difference is consistent with the observation that isopropoxyperfluorocyclooctatetraene has a tub inversion barrier several kcal/mol higher than its hydrocarbon counterpart.[13] Fluorine–fluorine nonbonded repulsions in the transition state are probably the principal reason for the higher barrier in both cases.

Finally, the rate constant for cyclization (k_c) of triene **3t** to **3d** was measured by the method of spin-saturation transfer, as described in the Experimental Section. At 102.(4) °C in toluene-d_8, k_c = 0.056 ± 0.003 s^{-1}; this corresponds to a free energy of activation of 24.3 kcal/mol. We can now construct a free energy diagram that includes three of the four interconverting species in the **3t**/**3d** system, as shown in Figure 4.

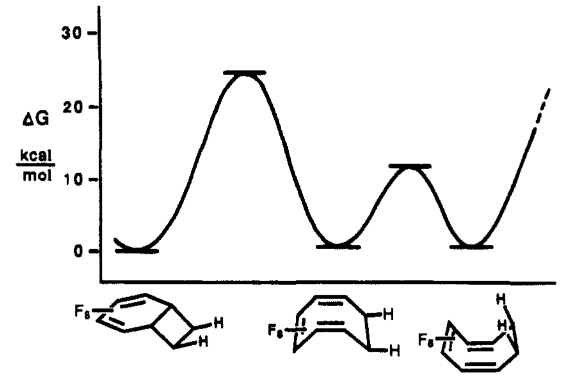

Figure 4. Free energy diagram for the **3d**–**3t** system. The measurements were made at rather different temperatures, as described, but entropy changes are small enough for the kinds of interconversions depicted that the diagram is essentially correct for ambient temperatures.

For the parent hydrocarbon **1t**, $\Delta G^{\ddagger}$ for cyclization is 27.0 kcal/mol at this temperature.[4] Since cyclization of **1t** is significantly endergonic while that of **3t** is slightly exergonic, the average of the barrier heights for the forward and reverse reaction provides a better basis for comparison of the free energies of activation of the two equilibrating systems. Computed this way, $\Delta\Delta G^{\ddagger}$ is just 2.0 kcal/mol.

A similar comparison can be made between cyclooctatetraene (**12**) and octafluorocyclooctatetraene (**14**). We have found that K_{eq} = 0.002 (8) ($\Delta G°$ = 3.4 kcal/mol) at 20 °C for cyclization of **14** to the bicyclo[4.2.0]octatriene **15**.[14] This measurement was made directly by ^{19}F NMR integration (relative to an internal area standard) of a sample in acetone-d_6, which had been pulsed for hours in order to bring the spectrum of the minor isomer out of the baseline.

12 R = H
14 R = F
13 R = H
15 R = F

Together with $\Delta G^{\ddagger}$ = 19.9 kcal/mol for ring opening of the bicyclic isomer at this temperature,[7] the free energy difference between **14** and **15** gives the value 23.3 for $\Delta G^{\ddagger}$ for cyclization. The average of the free energies of activation for forward and reverse reactions is thus 21.5 kcal/mol. The corresponding quantity for **12** and **13** is 23.8 kcal/mol,[16] and therefore $\Delta\Delta G^{\ddagger}$ = 2.3 kcal/mol at 20 °C. This $\Delta\Delta G^{\ddagger}$ and the 2.0 value from the preceding paragraph reveal that complete fluorine substitution on a hexatriene–cyclohexadiene system causes little change in the height of the barrier separating these valence isomers.

Some of the results we have presented bear on the thorny question of the strain energy of octafluorocyclobutane. Fundamental as that quantity is, estimates of it have varied from 24 kcal/mol *greater* than to 17.6 kcal/mol *less* than that of the parent hydrocarbon,[17] and the true value is still not known with accuracy.[18] The uncertainty arises from the difficulty of choosing appropriate model compounds and from the paucity of accurate thermochemical data on fluorocarbons. The free energy for cyclization of **4t** relative to **1t** and **2t** is a rough measure of the driving

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(10) Sanders, J. K. M.; Hunter, B. K. *Modern NMR Spectroscopy*; Oxford University Press: Oxford, 1987.

(11) The difference in repulsion energy between the two pairs of C–F bond dipoles in the exo and endo configurations is calculated to be several kcal/mol even with conservative values for the bond dipole moments.

(12) St. Jacques, M.; Prud'homme, R. *Tetrahedron Lett.* **1970**, 4833–6.

(13) Spector, T. Ph.D. Dissertation, Dartmouth College, 1987.

(14) For the parent hydrocarbon, K_{eq} = 0.0001 at 100 °C. See ref 15 and: Huisgen, R.; Mietzsch, F. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 83. More recently this equilibrium has been studied directly at very high temperatures: Squillicote, M. E.; Bergman, A. *J. Org. Chem.* **1986**, *51*, 3910.

(15) Huisgen, R.; Boche, G.; Dahmen, A.; Hechtl, W. *Tetrahedron Lett.* **1968**, 5215–9.

(16) This quantity is the average of 27.8 and 19.8 kcal/mol, the $\Delta G^{\ddagger}$'s at 20 °C for the cyclization and ring-opening reactions, respectively. See ref 15 and: Vogel, E.; Kiefer, H.; Roth, W. R. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 442.

(17) Smart, B. E. In *Molecular Structure and Energetics*; Liebman, J. F., Greenberg, A., Eds.; VCH Publishers: Deerfield Beach, FL 1986; Vol. 3, pp 141–91.

(18) Liebman, J. F.; Dolbier, W. R., Jr.; Greenberg, A. *J. Phys. Chem.* **1986**, *90*, 394–7.

force for cyclobutane ring formation which results from substitution of fluorines for hydrogen on the 4-ring carbons. For **1** as the model system, this $\Delta\Delta G^\circ = -5.4$ kcal/mol; for **2**, $\Delta\Delta G^\circ = -6.2$ kcal/mol (100 °C). These results are consistent with the view that octafluorocyclobutane enjoys less strain energy than cyclobutane itself but that the difference is not greater than several kcal/mol.

Conclusion

This investigation has revealed that complete substitution of fluorine for hydrogen on the triene system of a 1,3,5-cyclooctatriene brings about only modest change in either the equilibrium constant or the height of the barrier for cyclization, but that K_{eq} is influenced strongly by the extent of fluorination of the saturated carbons.[19] A much higher barrier for tub–tub interconversion was found in a highly fluorinated cyclooctatriene than in the parent hydrocarbon, probably for steric reasons. The exo and endo configurations of the derived bicyclic diene were found to differ considerably in energy, presumably because of differences in dipole–dipole repulsion. Evidence has been adduced that the controversial strain energy of octafluorocyclobutane is smaller than that of cyclobutane itself, but not dramatically so.

Experimental Section

Melting points were determined in open capillary tubes and are uncorrected. The ^{19}F NMR spectra were obtained at 282.2 MHz on a Varian XL-300 spectrometer or at 56.2 MHz on a JEOL FX60Q Fourier transform instrument with trichlorofluoromethane (Freon 11) as an internal standard. Chemical shifts are reported in parts per million upfield from the reference. ^{1}H NMR spectra and all ^{19}F decoupling, spin-saturation transfer, nuclear Overhauser enhancement, and equilibrium studies were performed on the XL-300. Analytical gas chromatograms were obtained with a Hewlett-Packard Model 5880A gas chromatograph with a methylsilicone capillary column, flame ionization detector, and electronic integration. Preparative gas chromatography was performed on a Hewlett-Packard Model 5750 instrument with a thermal conductivity detector, using a 10 ft × 0.25 in. column containing 10% SF-96 on 80/100 mesh Chromasorb-W AW-DMCS. Peak areas were not corrected for differential detector response. Mass spectra were determined with a Finnigan Model 4023 quadrupole mass spectrometer. Constant temperature was maintained with use of a Haake Model S bath with a Model F3 controller, accurate to ±0.01 deg. An air-driven Kugelrohr motor (Aldrich) was modified by interchanging the two gears, thus reducing its arc from 300 °C to about 20 °C, and was used as a rocking motor.

All solvents and reagents used in this work were reagent grade. Perfluorobenzene was purchased from Fairfield Chemical and ethylene from Matheson Gas Products. Toluene-d_8 was supplied by Stohler Isotope Chemicals and dodecane-d_{26} by Merck, Sharp and Dohme of Canada. Inorganic chemicals came from Fisher Scientific, and other organics were from Aldrich Chemical Co. Microanalytical data were obtained from Spang Microanalytical Laboratory, Eagle Harbor, MI.

Zinc dust was activated by stirring with 1 N hydrochloric acid for 5 minutes, washing with water, and drying under vacuum; it was stored under argon. Glass pyrolysis tubes were silated by adding a few drops of *N,O*-bis(trimethylsilyl)acetamide and heating the tube over a microburner flame in the hood while the liquid made contact with all inner surfaces; the tube was washed out with carbon tetrachloride and dried under vacuum.

1,2,3,4,5,6-Hexafluoro-*anti*-tricyclo[4.2.0.0^{2,5}]oct-3-ene (5). The apparatus was a photochemical reactor that comprised a cylindrical three-necked Pyrex vessel containing in its central neck a water-cooled quartz well that surrounded the source, a Hanovia 679A36 450-W medium-pressure mercury arc fitted with a Vycor filter. Two small flanking necks served as inlet and outlet for ethylene gas, which was introduced via Teflon tubing into the bottom of the reactor. The assembly was cooled externally as well as internally with cold water. Acetonitrile (80 mL) and hexafluorobenzene (32.0 mL, 51.8 g, 0.278 mol) were combined in the reactor and stirred magnetically. Ethylene was bubbled slowly through this solution for 0.5 h to saturate it, and then the lamp was turned on. Slow ethylene flow was maintained throughout the reaction. The quartz well was removed twice and cleaned to assure that the reaction was not impeded by a film of polymer. By the 16th day the extent of conversion of the hexafluorobenzene had exceeded 99%, as determined by ^{19}F NMR, and the irradiation was halted.

The orange-red solution was poured into ice-water (300 mL) and extracted with isopentane (3 × 50 mL); the combined organic layers were then washed with water (50 mL) and dried over sodium sulfate. Isopentane was removed by distillation, leaving a good yield of colorless crystalline solid, mp 38–40 °C. The distillation should be performed carefully, as the product is quite volatile. After purification by recrystallization at ca. −25 °C from a minimum quantity of methanol and sublimation at room temperature (75–80 Torr), the tricyclooctene melted at 40.5–41.5 °C. IR (C_2Cl_4) 3000 (w), 1745 (s), 1440 (w), 1370 (s), 1290 (m), 1215 (m), 1190 (m), 1105 (m), 1070 (m), 990 (w), 955 (m), 865 (w), 820 cm^{-1} (m). Anal. Calcd for $C_8H_4F_6$: C, 44.87; H, 1.88; F, 53.24. Found: C, 44.80; H, 1.85; F, 53.36.

1,2,3,4,5,6-Hexafluorocycloocta-1,3,5-triene and 1,2,3,4,5,6-Hexafluorobicyclo[4.2.0]octa-2,4-diene (2). In a silated Pyrex ampule tricyclooctene **5** (85 mg, 0.40 mmol) and finely divided calcium carbonate (14 mg, 0.14 mmol) were combined. The ampule was cooled to 77 K, evacuated to 25 mTorr, and sealed. It was then heated at 160 °C for 22 h with rocking. ^{19}F NMR analysis of the liquid product revealed that it was 97% monocyclic (**2**t), 2% bicyclic (**2d**), and 1% starting material. The equilibrating **2t**/**2d** mixture was purified by preparative GC (injector, 160 °C; column, 147 °C; detector, 200 °C; retention time, 20 min). IR (neat) 2930 (w), 2860 (w), 1753 (m), 1700 (s), 1445 (s), 1380 (s), 1355 (s), 1320 (s), 1280 (m), 1235 (m), 1210 (s), 1190 (s), 1185 (m), 1105 (s), 1085 (s), 1040 (s), 980 (s), 940 (s), 840 cm^{-1} (s).

1-Fluoro-2-(pentafluorophenyl)ethane (9). Tricyclooctene **5** (390 mg, 1.8 mmol) was sealed as above in an untreated Pyrex ampule without any calcium carbonate present. The ampule was heated at 180 °C for 20 h, giving **9**. ^{19}F NMR ($CDCl_3$) 143.9 ($F_{3'}$, $F_{5'}$), 156.4 ($F_{4'}$), 162.9 ($F_{2'}$, $F_{6'}$), 218.4 ppm (F_1). IR (neat) 2978 (m), 2917 (m), 1657 (m), 1515 (s), 1477 (m), 1440 (w), 1427 (w), 1388 (m), 1348 (w), 1300 (m), 1255 (w), 1217 (w), 1134 (s), 1083 (m), 1047 (s), 1009 (s), 962 (s), 907 (s), 859 cm^{-1} (m). MS, *m/e* 214 (M^+), 195 ($M^+ - F$), 181 ($M^+ - CH_2F$).

3,4-Dichlorodecafluoro-*anti*-tricyclo[4.2.0.0^{2,5}]octane. To 7,8-dichlorooctafluoro-*anti*-tricyclo[4.2.0.0^{2,5}]oct-3-ene[6] (8.85 g, 27.8 mmol) was added 150 mL of Freon 113 (1,1,2-trichlorotrifluoroethane) in a three-necked 250-mL round-bottomed flask. The solution was maintained at 0 °C as a 1:1 fluorine–helium mixture was bubbled through it at approximately 4 mL/min. [The reaction also proceeds smoothly with a 1:4 mixture of fluorine and helium, which is safer to work with.] Reaction was monitored by observing the disappearance of the intense, sharp double bond stretching band at 1663 cm^{-1}. When the addition was complete (2 h), the solvent was removed by distillation at atmospheric pressure and the residue was purified by vacuum transfer (yield >90%). ^{19}F NMR ($CDCl_3$) 106.0, 111.0, 113.4, 118.9, 123.7, 127.8, 163.9, 179.5, 186.9, 188.5 ppm. Anal. Calcd for $C_8Cl_2F_{10}$: C, 26.91; H, 0.00; F, 53.22; Cl, 19.86. Found: C, 26.74; H, 0.13; F, 52.83; Cl, 20.02.

Decafluoro-*anti*-tricyclooct-3-ene (6). A. Via Dechlorination. A 50-mL round-bottomed flask with septum-capped side tubulation was attached by rubber vacuum tubing through a U-trap to a vacuum line. In the flask was placed 3,4-dichlorodecafluoro-*anti*-tricyclo[4.2.0.0^{2,5}]-octane (1.74 g, 4.87 mmol), activated zinc dust (1.05 g, 16.1 mmol), and dimethyl sulfoxide (30 mL). The mixture was subjected to 2 freeze–pump–thaw cycles, and the flask was then attached to the rocking motor and immersed in the ultrasonic bath. The U-trap was cooled in liquid nitrogen, and the pressure in the system was maintained at approximately 20 Torr while the flask was rocked and subjected to sonication. Reaction progress and product transfer were monitored by ^{19}F NMR analysis of aliquots withdrawn through the septum. Dechlorination began immediately and was complete in 20–30 min; collection of the product in the U-trap was complete after 2.5 h. Yield: 0.79 g, 57%. IR (CCl_4) 1758, 1370, 1334, 1298, 1203, 1068, 903 cm^{-1}. MS, *m/e* 286 (M^+), 267 ($M^+ - F$), 217 ($M^+ - CF_3$), 186 ($C_6F_6^+$, base), 124 ($C_4F_4^+$), 117 ($C_5F_3^+$), 100 ($C_2F_4^+$), 93 ($C_3F_3^+$).

B. Via Cycloaddition. A cylindrical quartz vessel (12 mm o.d. × ~500 mm) with an extension tube having a graded quartz/Pyrex seal was evacuated and filled with argon. Hexafluorobenzene (4.0 mL, 6.5 g, 35 mmol) was injected into the tube and degassed by the freeze–pump–thaw procedure. Tetrafluoroethylene was transferred into a graduated centrifuge tube cooled in liquid nitrogen, allowed to melt (3.3 mL, ~6 g, ~60 mmol), and statically vacuum transferred onto the hexafluorobenzene. In similar fashion 17 mL (measured at ca. −20 °C) of Freon 114 (1,2-dichlorotetrafluoroethane) was introduced into the vessel, which was then sealed in vacuo. After being thawed from the top down in order to avoid excess pressure buildup, the three components were mixed, and irradiation was begun in a cylindrical-cavity photoreactor equipped with ten 25-W low-pressure mercury lamps. The tube contents were mixed periodically during the course of the reaction. Within several hours a film of polytetrafluoroethylene formed on the walls of the vessel. After 143 h, the tube was cooled in dry ice and

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(19) Huisgen found striking and puzzling effects of substituents at the 7 and 8 positions on the equilibrium constant for cycloocta-1,3,5-triene cyclization (ref 15).

opened; the reaction mixture was transferred into a precooled distillation apparatus, and the volatile solvent (bp 4 °C) was taken off through a Podbielniak column having a nichrome spiral. GC analysis of the pot residue indicated that the yield of tricyclooctene **6** was 31%. Higher boiling than hexafluorobenzene, **6** nonetheless had much shorter GC retention times, e.g. on a 10% SF-96 column. The tricyclooctene could be purified by distillation through a small spinning band column, but clean separation from unreacted hexafluorobenzene was not achieved this way.

Decafluorobicyclo[4.2.0]octa-2,4-diene (4d). Tricyclooctene **6** (0.39 g, 1.36 mmol) was injected through a septum into an argon-filled heavy-walled glass ampule and frozen in liquid nitrogen. The ampule was evacuated and sealed and then heated for 12 h at 175 °C to give diene **4t** as a colorless liquid in quantitative yield. IR (CCl_4) 1744, 1695, 1400, 1356, 1264, 1208, 1020, 928, 842, 706 cm^{-1}. MS, *m/e* 286 (M^+), 217 ($M^+ - CF_3$), 186 ($C_6F_6^+$, base), 117 ($C_5F_3^+$). Anal. Calcd for C_8F_{10}: F, 66.43. Found: F, 66.67.

3,4-Dichloro-1,2,3,4,5,6,7,8-octafluoro-*anti*-tricyclo[4.2.0.0^{2,5}]octane. A stirred suspension of 10% palladium-on-charcoal (1.11 g) in 200 mL of isopentane in a 500-mL three-necked, round-bottomed flask was saturated with hydrogen at 0 °C in an atmospheric pressure hydrogenation apparatus. Neat tricyclooctene **7** (10.34 g, 32.4 mmol) was added in one portion via syringe. Stirring was continued at 0 °C, and after 4 h 810 mL (1 equiv) of hydrogen had been absorbed. The apparatus was purged with nitrogen, the suspension was suction filtered through a filter-aid pad, and isopentane was removed from the filtrate by distillation at atmospheric pressure. A colorless liquid was collected at 55–75 °C (18 Torr); yield, ~7.4 g (71%). ^{19}F NMR ($CDCl_3$) 108.0, 117.0, 125.7 (2 F total); 167.7, 168.8, 178.2, 180.1, 186.0, 204.7 ppm (6 F total). ^1H NMR ($CDCl_3$) 5.56 (m). IR (neat) 1362, 1302, 1205, 1145, 980, 795 cm^{-1}. MS, *m/e* 285 ($M^+ - Cl$), 256 ($M^+ - C_2H_2F_2$), 160 ($C_7F_7^+$, base).

1,2,3,4,5,6,7,8-Octafluoro-*anti*-tricyclo[4.2.0.0^{2,5}]oct-3-ene (8). Activated zinc dust (7.6 g, 0.12 mol) and dimethyl sulfoxide (150 mL) were placed in a 250-mL three-necked round-bottomed flask. 3,4-Dichloro-1,2,3,4,5,6,7,8-octafluoro-*anti*-tricyclo[4.2.0.0^{2,5}]octane (10.0 g) was added dropwise via addition funnel as the mixture was rocked and sonicated in an experimental setup like that described for the preparation of **6**. NMR monitoring revealed that the product was formed quickly, but very little of it distilled into the cold trap even at pressures below 0.5 Torr where solvent begins to distill at room temperature. Thus, the reaction mixture was poured into cold water and the product was extracted with ether. The ether layer was dried over potassium carbonate, filtered, and stripped carefully on the rotary evaporator to give a colored solid/liquid mixture (~5 g). A vacuum transfer left the color behind, yielding a solid that was quite pure by GC. Combined yield, 3.2 g (41%). Upon further purification by preparative GC, the olefin had mp 92–92.5 °C. IR (CCl_4) 1758 cm^{-1}. MS, *m/e* 249 ($M^+ - 1$), 231 ($M^+ - F$), 186 ($C_6F_6^+$). Anal. Calcd for $C_8H_2F_8$: C, 38.42; H, 0.80; F, 60.96. Found: C, 38.09; H, 0.81; F, 60.77.

***cis*-1,2,3,4,5,6,7,8-Octafluorocycloocta-1,3,5-triene and *endo*,*cis*-1,2,3,4,5,6,7,8-Octafluorobicyclo[4.2.0]octa-2,4-diene (3).** Tricyclooctene **8** and one-third its weight of calcium carbonate were sealed in vacuo in a silated Pyrex ampule and heated at 160 °C for 15 h. The mixture of valence isomers **3** was obtained in essentially quantitative yield. IR (toluene-d_8) 2957, 1745, 1722, 1687, 1360, 1320, 1215, 974, 942, 886 cm^{-1}. MS, *m/e* (for each isomer) 250 (M^+), 212 ($M^+ - F_2$), 199 ($M^+ - CHF_2$), 186 ($C_6F_6^+$, base), 181 ($C_7H_2F_5^+$), 161 ($C_7HF_4^+$), 117 ($C_3F_3^+$).

Determination of the Equilibrium Constant for 4t $\rightleftharpoons$ 4d. Four samples of decafluorobicyclo[4.2.0]octa-2,4-diene (**4d**), several milligrams apiece, were sealed in melting point tubes in vacuo. They were heated in a constant temperature bath at 100 °C for 1.5 h and then instantly quenched in a dry ice/acetone bath. About 0.5 μL of each sample was injected into the analytical gas chromatograph (inj. 54°, det. 150 °C, col. 21 °C), and the ratio of monocyclic to bicyclic peak area was measured. The monocyclic isomer **4t** had a slightly longer retention time than **4d**, as expected by analogy to related cyclooctatriene/bicyclooctadiene systems, and baseline resolution was achieved under these conditions. The peak area ratios varied from 0.0052 to 0.0055 and the average value was 0.0053, corresponding to K_{eq} = 18 (5) for **4t** $\rightleftharpoons$ **4d**.

For this experiment to be valid the equilibrium time must be adequate, the quenching of the equilibrated samples must be effectively instantaneous, and the GC conditions must be mild enough that no equilibration occurs during analysis. Prior to the experiment described above, measurements were made over a range of equilibrium temperatures and GC conditions to assure that all three criteria were met.

Spin-Saturation Transfer Rate Measurements on Triene 3t. These ^{19}F NMR measurements were carried out at 282 MHz on a solution of triene **3t** (80 mg) in toluene-d_8 (0.3 mL) at 102.(4) °C. A triene signal was saturated by using the spin decoupler for a sufficient period of time (21 s) to reach spin population equilibrium, and then an observe pulse followed. This sequence was performed multiple times before Fourier transformation in order to obtain an accurate measurement of the intensity of the corresponding signal in the diene, the equilibrium magnetization H_{eq}. The whole experiment was repeated with the decoupler on for only a short interval (D) before the observe pulse, and with a sufficient delay between repetitions to permit complete spin relaxation. Again the diene signal intensity (H_t) was measured. This experiment was carried out for several incremented values of the decoupler on-time (1, 3, 6, 10, and 15 s). Each of the experiments that have been described were repeated three times, and average values were used to construct a plot of ln ($H_t - H_{eq}$) versus D. A straight line (correlation coefficient, 1.00) of slope $-1/\tau_1$ was obtained, where τ_1 = 6.74 s is the *apparent* relaxation time of the diene resonance. From the relation $H_{eq}T_1 = H_0\tau_1$, where H_0 is the signal intensity in the absence of decoupling, the relaxation time in the absence of exchange, T_1, was found to be 10.8 s. The equation $k_c = 1/\tau_1 - 1/T_1$ yielded the rate constant for cyclization, k_c = 0.056 s^{-1}, with estimated error ±0.003 s^{-1}.

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Registry No. **2d**, 127399-53-5; **2t**, 127399-54-6; **3d**, 127399-55-7; **3t**, 127399-56-8; **4d**, 127399-57-9; **4t**, 127399-58-0; **5**, 127399-59-1; **6**, 127421-14-1; **7**, 72726-96-6; **8**, 127399-60-4; **9**, 127399-61-5; $H_2C{=}CH_2$, 74-85-1; $F_2C{=}CF_2$, 116-14-3; hexafluorobenzene, 392-56-3; 3,4-dichlorodecafluoro-*anti*-tricyclo[4.2.0.0^{2,5}]octane, 127399-62-6; 3,4-dichloro-1,2,3,4,5,6,7,8-octafluoro-*anti*-tricyclo[4.2.0.0^{2,5}]octane, 127399-63-7.