4292 J. Org. Chem. 1980, 45, 4292–4295

Registry No. **1a**, 74542-27-1; **1b**, 625-33-2; **1c**, 141-79-7; **1d**, 80-62-6; **1e**, 932-66-1; (*Z*)-**1f**, 7417-54-1; (*E*)-**1f**, 7417-55-2; (*Z*)-**1g**, 43142-59-2; (*E*)-**1g**, 43142-58-1; **1h**, 825-25-2; **1i**, 89-82-7; **1j**, 74542-28-2; **1k**, 74542-29-3; **1l**, 1121-18-2; **2a** (isomer 1), 74542-30-6; **2a** (isomer 2), 74561-77-6; **2b**, 74542-31-7; **2c**, 62407-64-1; **2d**, 74542-32-8; **2e**, 74542-33-9; **2f**, 74542-34-0; **2g**, 74542-35-1; **2h**, 74542-36-2; **2h′**, 74542-37-3; **2i** (epimer 1), 62407-65-2; **2i** (epimer 2), 62446-39-3; **2j**, 74542-38-4; (*Z*)-**2k**, 74552-05-9; (*E*)-**2k**, 74542-39-5; **2l**, 74552-06-0; **3c**, 74552-07-1; **3h**, 74552-08-2; **3h′**, 74542-40-8; **4d**, 74542-41-9; **4e**, 74542-42-0; 1-(trimethylsiloxy)cyclohexene, 6651-36-1; 1,1,1-trifluoroacetone, 421-50-1; (*R*,*R*)-2-(1-hydroxy-1-methyl-2,2,2-trifluoroethyl)cyclohexanone, 74542-43-1; (*R*,*S*)-2-(1-hydroxy-1-methyl-2,2,2-trifluoroethyl)cyclohexanone, 74542-44-2; PTAD, 4233-33-4.

Configurations and Chemistry of the Perfluorotricyclo[4.2.0.0^{2,5}]octa-3,7-dienes

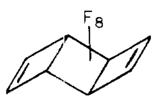
A. C. Barefoot, III, W. D. Saunders, John M. Buzby, M. W. Grayston, and D. M. Lemal*

Department of Chemistry, Dartmouth College, Hanover, New Hampshire 03755

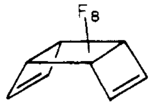
Received November 13, 1979

Irradiation at 2537 Å of perfluorocyclooctatetraene yielded *anti*- and *syn*-perfluorotricyclo[4.2.0.0^{2,5}]octa-3,7-dienes **1a** and **1b**, respectively, which reverted quantitatively to the tetraene at 150 °C. Bromine addition occurred exclusively in the exo, suprafacial fashion with both dienes, but only the anti isomer added 2 mol of bromine. The latter fact, together with analysis of the ^{19}F NMR spectra of the bromine adducts, constitutes convincing evidence for the configurational assignments for **1a** and **1b**. Perfluorobenzene underwent [2 + 2] photocycloaddition with chlorotrifluoroethylene, and the bicyclic adducts suffered photochemical electrocyclization to a stereoisomeric mixture of 7-chlorotricyclo[4.2.0.0^{2,5}]oct-3-enes. Analysis of the ^{19}F NMR spectra of the major isomers permitted their assignment as exo,anti and endo,anti. Reduction of the former gave **1a**, thus confirming the diene's configuration. An explanation based on "second-order" orbital symmetry effects is suggested for the syn/anti stereoselectivity found in the thermal and photochemical electrocyclic processes described above.

Irradiation of perfluorocyclooctatetraene[1,2] in the vapor phase at 2537 Å in an atmosphere of nitrogen yields a 20:1 mixture of the stereoisomeric title compounds.[3] They are volatile crystalline solids melting at 40–41.5[5] and 51–53 °C, respectively, which revert cleanly to their progenitor when heated at 150 °C.[6] Assignment of configuration to this pair of dienes is required for understanding the photochemistry of perfluorobenzene as well as perfluorocyclooctatetraene, as will become apparent. The chemistry of the dienes and analysis of the ^{19}F NMR spectra of various derivatives have revealed clearly which is anti (**1a**) and which syn (**1b**). These matters form the substance of the present report.



1a

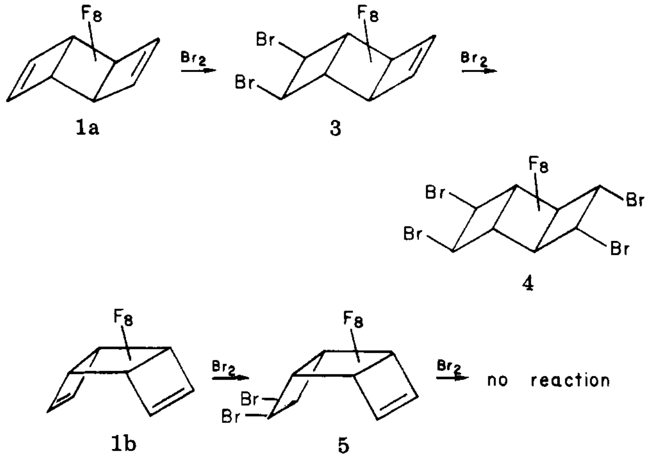


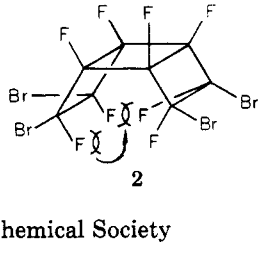
1b

Results and Discussion

Bromine Adducts. Each diene reacts smoothly with bromine in carbon tetrachloride at room temperature to give a single dibromide. The higher melting diene reacts about 3 times as fast as the lower, but the reaction ceases abruptly after consumption of 1 mol of bromine. In contrast, the dibromide formed from the 41 °C isomer adds a second mole easily enough that tetrabromide accompanies the dibromide before the starting diene is fully consumed, even when the reaction is carried out at −20 °C. These facts are easily understood if, and only if, *the low-melting isomer has the anti and the high-melting diene the syn configuration.* Models confirm that the double bond of a dibromide derived from **1a** can be comparably reactive to those of **1a** itself but that the double bond of a dibromide formed from **1b** should powerfully resist further addition. Even the least strained tetrabromide **2**

Scheme I





2

---

[1] M. G. Gerace, D. M. Lemal, and H. Ertl, *J. Am. Chem. Soc.*, **97**, 5584 (1975).

[2] D. M. Lemal, J. M. Buzby, A. C. Barefoot, III, M. W. Grayston, and E. D. Laganis, *J. Org. Chem.*, **45**, 3118 (1980).

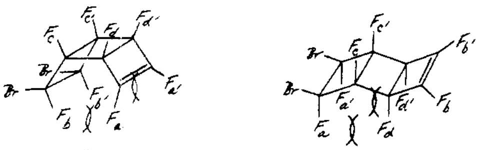
[3] Formation of tricyclo[4.2.0.0^{2,5}]octa-3,7-dienes by ultraviolet irradiation of a cyclooctatetraene is highly unusual, but it finds a precedent in the behavior of perfluorooctamethylcyclooctatetraene.[4]

[4] L. F. Pelosi and W. T. Miller, Jr., *J. Am. Chem. Soc.*, **98**, 4311 (1976).

[5] The lower melting isomer has been reported as the product of vapor-phase photolysis of tetrafluorocyclobutene-3,4-dicarboxylic anhydride in an atmosphere of nitrogen.[1] Contrary to the original interpretation, it is now clear that most, if not all, of the tricyclooctadiene is formed in this experiment by photocyclization of perfluorocyclooctatetraene (which is dramatically accelerated by an inert gas).

[6] This behavior parallels that of their hydrocarbon counterparts. (a) M. Avram, I. G. Dinulescu, E. Marica, G. Mateescu, E. Sliam, and C. D. Nenitzescu, *Chem. Ber.*, **97**, 382 (1964). (b) H. M. Frey, H.-D. Martin, and H. Hekman, *J. Chem. Soc., Chem. Commun.*, 204 (1975).

0022-3263/80/1945-4292$01.00/0



5 3

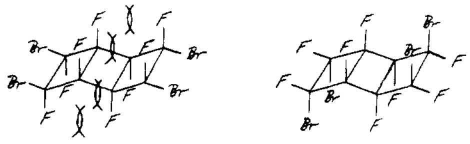
Figure 1. ^{19}F NMR assignments and "through-space" interaction in the syn and anti dibromides **5** and **3**.

which could be derived from **1b** (without skeletal rearrangement) would suffer from extremely severe F–F nonbonded repulsions. Clearly, the syn/anti assignments must be correct whatever the stereochemistry of bromine addition to **1a** and **1b** may be.

Since the centrosymmetric anti diene **1a** must have a vanishing dipole moment, unlike its syn counterpart, the fact that the 41 °C isomer has the shorter GLC retention time is in harmony with the anti assignment. Thermal isomerization to perfluorocyclooctatetraene of the syn isomer is ~8 times as fast as that of the anti form at 150 °C ($t_{1/2}^{\mathrm{anti}} \approx 0.5$ h, gas phase). In the parent hydrocarbons also, the syn is the more labile isomer, a fact which Frey has attributed to greater strain in the syn skeleton.[6b]

As it happens, all three additions of bromine alluded to above occur suprafacially exo. Their suprafacial character is apparent from the presence of only four sets of chemical-shift-distinguishable fluorines in the dibromides **3** and **5** and only two sets in the tetrabromide **4** (see Scheme I). The fact that addition is cleanly (and unconventionally[7]) suprafacial is a clue that steric hindrance is influencing the reaction course; indeed, models reveal that the endo faces of the double bonds of **1a** as well as **1b** are shielded from an attacking reagent. The conclusion that all of the bromines in **3–5** are disposed exo is confirmed by analysis of the ^{19}F NMR spectra of these compounds, as explained below.

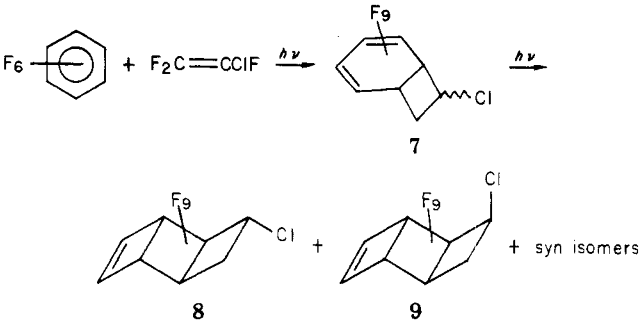
For reference, the ^{19}F NMR spectra (in CCl_4) of the low- and high-melting tricyclooctadienes comprise symmetrical multiplets at, respectively, δ 118.2 and 113.2 (vinyl F's) and δ 182.13 and 197.07 (bridgehead F's).[8] Syn dibromide **5** gives a spectrum (in CCl_4) with multiplets at δ 110.27, 120.50, 167.16, and 184.42. Here and throughout this paper the NMR resonances of a compound will be designated alphabetically, beginning at low field. The high-field signals (F_c and F_d) of **5** are in the region for bridgehead fluorines and can be assigned as shown in Figure 1 by analogy to the chemical shifts of the bridgehead fluorines in **1a** and **1b**. Decoupling experiments reveal that the "d" fluorines are coupled much more strongly to the "a" than to the "b" fluorines, thus permitting one to complete the assignments as shown. The considerably greater signal breadths of the low-field pair of signals indicate that the vinyl fluorines are coupled rather strongly to those geminal to bromine, a conclusion confirmed by decoupling experiments ($J_{ab} \approx 25$ Hz).[9] This observation points to the "through-space" interaction depicted in Figure 1 and confirmed by models. One would have expected the five- (and six) bond coupling between these pairs of fluorines to be small if the bromines had been endo.[10]



4 6

Figure 2. Comparison of configurations **4** and **6**.

Scheme II



Anti dibromide **3** shows ^{19}F NMR multiplets (in $CDCl_3$) at δ 117.20, 118.73, 157.61, and 185.73. As in the spectrum of **5**, the bridgehead fluorines vicinal to bromine are shifted dramatically downfield from their location in the diene spectrum. The "d" signal is much broader than the "c" signal due in part to coupling with the "b" fluorines but principally to strong coupling with the "a" fluorines ($J_{ad} \approx 35$ Hz).[11] This new, strong coupling developed as a consequence of bromination is easily understood in through-space terms, for models reveal significant overlapping of van der Waals radii of the "a" and "d" fluorines of **3** when they are assigned as in Figure 1. Had bromine added endo, a much smaller four-bond interaction between these pairs of fluorines would have been expected.[12]

The two multiplets of equal area at δ 113.80 and 157.23 (in CCl_4) which comprise the ^{19}F NMR spectrum of tetrabromide **4** are very broad (width at half height $\simeq$60 Hz), revealing strong coupling between the A and X (bridgehead) sets in this AA'A''A'''XX'X''X''' spectrum. Had the tetrabromide possessed the alternative configuration **6**, coupling between the A and X sets comparable to the small coupling[13] between the similarly arrayed sets of bridgehead fluorines in syn dibromide **5** should have been found (Figure 2).

To recapitulate, mechanistic reasoning based on steric hindrance to bromine attack and product structure analysis based on through-space F–F coupling conspire to force the conclusion that the products of bromine addition to tricyclooctadienes **1a** and **1b** all have exo configurations (**3–5**). Outside of the stereochemistry, there is no evidence available regarding the mechanism of bromination of dienes **1a** and **1b**. Considering the electron deficiency of these molecules, however, we are biased in favor of a free radical chain process.[14]

Perfluorobenzene/Olefin Photoadducts. When a neat liquid mixture of perfluorobenzene and chlorotri-

---

(7) F. Freeman, *Chem. Rev.*, **75**, 439 (1975).

(8) All ^{19}F chemical shifts are reported in parts per million upfield from internal $CFCl_3$.

(9) For comparison, the half-height of the "c" multiplet of **5** is narrowed by only ~2 Hz upon irradiation of the "b" signal.

(10) A very extensive and useful compilation of F–F coupling constants, accompanied by an account of the underlying theory, is found in J. W. Emsley, L. Phillips, and V. Wray, "Fluorine Coupling Constants", Pergamon Press, Oxford, 1977 (reprinted from *Prog. Nucl. Magn. Reson. Spectrosc.*, **10**, 83–756 (1976).

(11) In a family of highly fluorinated bicyclo[2.2.1]heptane derivatives, coupling constants between endo-oriented C(2) and C(6) fluorines fall in the range of 45–84 Hz by virtue of "through-space" interaction. See J. W. Emsley, L. Phillips, and V. Wray, *Prog. Nucl. Magn. Reson. Spectrosc.*, **10**, 471, 472, 474–477 (1976).

(12) Even if the assignments of the bridgehead fluorines were switched, the large coupling would not be consistent with endo bromines, as an argument in the next paragraph of text makes clear.

(13) The half-height width of the "c" signal for **5** is <8.0 Hz in $CDCl_3$.

(14) For a discussion of mechanisms for addition of halogens to fluorinated olefins, see B. L. Dyatkin, E. P. Mochalina, and I. L. Knunyants in "Fluorine Chemistry Reviews", Vol. 3, P. Tarrant, Ed., Marcel Dekker, New York, 1969, p 45.

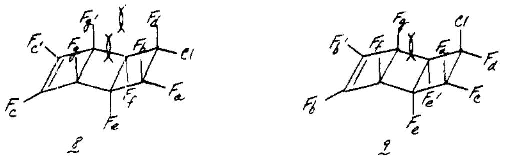


Figure 3. ^{19}F NMR assignments and "through-space" interaction in photoadducts 8 and 9.

fluoroethylene was irradiated at 2537 Å, a [2 + 2] cycloaddition occurred to give, initially, both stereoisomers of 7 (Scheme II); under the reaction conditions most of the 7 photocyclized to yield a stereoisomeric mixture of tricyclic olefins,[15,16] two of which predominated heavily over the remaining two possibilities. The major isomers were obtained pure by preparative GLC and were assigned the exo,anti (8) and endo,anti (9) configurations as explained below.

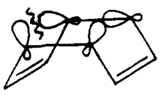
The ^{19}F NMR spectrum ($CDCl_3$) of 8, the isomer of longer retention time, comprises the following signals: δ 112.3 (slightly subsplit AB doublet, $J_{ab} \simeq 214$ Hz, F_a, Figure 3), 115.4 (subsplit AB doublet with high-field portion obscured, $J_{bg} \simeq 28$ Hz, F_b), 118.3 (narrow m, F_c, $F_{c'}$), 124.8 (slightly subsplit doublet, $J_{dg'} \simeq 38$ Hz, F_d), 170.1 170.1 (m, F_e), 182.0 (m, F_f), 185.9 (m, F_g, $F_{g'}$). The spectrum divides roughly into upfield and downfield portions, with the former clearly attributable to the four bridgehead fluorines (F_e–$F_{g'}$). A coupling of ~214 Hz immediately identifies the geminal fluorines (F_a, F_b), so assignment of the two-fluorine signal to the virtually equivalent olefinic fluorines (F_c, $F_{c'}$) and the remaining doublet to the fluorine geminal to chlorine (F_d) is straightforward. Key to the assignment of stereochemistry are the ~25- and ~38-Hz couplings which reveal that one of the geminal fluorines (F_b) and F_d each interact strongly with a single bridgehead fluorine. This is reasonable only in the exo,anti configuration, where these pairwise interactions are again obvious from the considerable overlap of van der Waals radii. Reduction of 8 with zinc in acetic acid yielded the 41 °C tricyclooctadiene, thereby confirming the anti configuration of the latter.

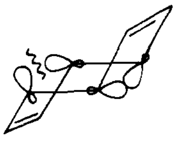
Turning now to isomer 9, one finds that its rather similar ^{19}F spectrum can be interpreted in parallel fashion. Now, however, only a single fluorine of the downfield set, a member of the geminate pair, experiences strong coupling ($J \simeq 34$ Hz) to a bridgehead fluorine. This observation is consistent only with the endo, anti configuration: ^{19}F NMR ($CDCl_3$) δ 109.6 (subsplit AB d, $J_{ac} \simeq 219$ Hz, $J_{af} \simeq 34$ Hz, F_a), 118.1 (m, F_b, $F_{b'}$), 125.1 (AB d, F_c), 133.0 (br s, F_d), 180.8 (m, F_e, $F_{e'}$), 186.0 (m, F_f), 188.6 (m, F_g).

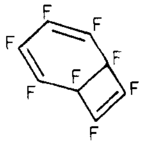
The properties of 8 and 9 are nicely in accord with the assigned configurations. The longer GLC retention time of 8 relative to 9 makes sense in terms of the greater accessibility of the polarizable chlorine atom in 8. Whereas zinc reduction of 8 is facile, 9 is stoutly resistant to attack,[17] an observation which implies a surprisingly large steric effect on a dissolving-metal reduction.

Dynamic Considerations. If Frey is correct in ascribing greater strain to the syn than to the anti tricyclooctadiene skeleton,[6b] the preferential formation of anti product in the photocyclization of perfluorocyclooctatetraene and perfluorobenzene–olefin adducts (7) may simply be dictated by product stability considerations. It is tempting to speculate, however, that more subtle factors may be at work in these transformations.

Considering first the thermal ring opening of the perfluorotricyclooctadienes and assuming that their rigid geometry requires the (forbidden) disrotatory pathway for cyclobutene cleavage, one discovers a potentially significant difference between the transition states 10 and 11 for the isomerization of 1b and 1a, respectively, to the bicyclic isomer 12. In 10 the atomic orbitals comprising the cleaving σ bond overlap substantially with those forming the other strained and bent bridging bond, but the corresponding sets of orbitals in 11 are nearly orthogonal. That the effect of this overlap in 10 should be stabilizing is clear when one recognizes that it confers some six-electron, aromatic character on an otherwise four-electon, antiaromatic transition state.[18] The faster ring opening observed for 1b relative to 1a may well be ascribable to this interaction.


10


11



12

From the well-documented complementarity of ground-state vs. excited-state electrocyclic processes,[20] it follows that photocyclization of perfluorobicyclo[4.2.0]-octa-2,4,7-triene (12)[21] should lead preferentially to *anti*-tricyclooctadiene, the isomer found to predominate heavily. Although there is not yet convincing experimental evidence that 12 is the actual precursor of 1 in the photochemistry of perfluorocyclooctatetraene, we regard its intermediacy as very likely indeed.[22]

Experimental Section[24]

***anti*- and *syn*-Perfluorotricyclo[4.2.0.0^{2,5}]octa-3,7-dienes (1a,b).** Perfluorocyclooctatetraene[2] (3.46 g, 14.0 mmol) was vacuum transferred into a 5-L cylindrical quartz vessel which was then pressurized to ~600 torr with nitrogen dried at −196 °C. The vessel was mounted in a cylindrical photoreactor fitted with ten 25-W General Electric G25T8 low-pressure mercury lamps and irradiated for 24 h. The product mixture was slowly pumped out of the reaction vessel and into a glass-helix-packed, −196 °C U-trap which was followed by a second, unpacked −196 °C trap. After the packed trap had been warmed to permit transfer of

---

(15) The analogous photocycloaddition of perfluorobenzene to 1,2-dichloro-1,2-difluoroethylene forms the basis of a practical synthesis of perfluorocyclooctatetraene, described in ref 2.

(16) For a review of photocycloadditions of perfluorobenzene, see M. Zupan, *Isr. J. Chem.*, 17, 92 (1978).

(17) Starting material was recovered after heating for 10 h at 80 °C with excess zinc dust in diethylacetic acid.

(18) Firm control of ring-opening stereochemistry by a bent cyclobutane bond is nicely illustrated by Berson's study[19] of the thermal decomposition of *syn,cis*- and *syn, trans*-2,5-dimethyl-1,3-diazabicyclo-[4.2.0]oct-3-ene. Unlike the present case, in which the bent bond is proposed to have a "second-order" effect, that bond is broken in the azo compound thermolyses.

(19) J. A. Berson, E. W. Petrillo, Jr., and P. Bickart, *J. Am. Chem. Soc.*, 96, 636 (1974).

(20) See, for example, R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Academic Press, New York, 1970.

(21) As in the hydrocarbon series, the bicyclic triene apparently exists in thermal equilibrium with the stabler monocyclic tetraene. To date it has escaped direct detection, but Diels-Alder adducts prepared from the tetraene are formally (and almost certainly in reality) derived from the bicyclic valence isomer (B. B. Seiders and R. C. Petter, unpublished work in our laboratory).

(22) The bicyclic valence isomer 12 may be formed photochemically as well as thermally; this is the case with cyclooctatetraene itself.[23] Pelosi and Miller have proposed the bicyclic species as an intermediate in the photointerconversion of perfluorooctamethylcyclooctatetraene with its tricyclo[4.2.0.0^{2,5}] isomers.[4]

(23) G. J. Fonken, *Chem. Ind.* (*London*), 1625 (1963); E. Migirdicyan and S. Leach, *Bull. Soc. Chim. Belg.*, 71, 845 (1962).

(24) Since the ^{19}F NMR spectra of all compounds are presented in the Results and Discussion, no NMR data appear below.

products to the second trap, the latter was warmed to −78 °C and then isolated from the vacuum manifold. Its contents were transferred in vacuo into a small storage bulb (3.22 g, 93%). A portion (0.943 g) of the colorless, largely crystalline product was vacuum transferred at room temperature into a second vessel. GLC analysis on a 10 ft × $^1/_4$ in., 20% SF-96 on HMDS treated Chromasorb W column at 50 °C with a flow rate of 160 mL/min revealed that the newly transferred fraction was considerably enriched in the syn isomer (~20%), while the residue was virtually pure anti diene (retention times 165 and 130 s, respectively). Pure syn isomer (101 mg) was obtained by GLC trapping. In other runs, GLC analysis of the total product mixture had shown a 20:1 ratio of anti to syn diene.

The UV spectra of **1a** (cyclohexane) and **1b** (vapor phase) displayed end absorption only; their mass spectra each showed a parent peak at *m/e* 248, with the base peak at *m/e* 179 (− CF_3); for **1a** IR (vapor) 1744 (FC=CF), 1369 (CF), 1214, 1101, 891, 814 cm^{-1}; for **1b** IR (vapor) 1753 (FC=CF), 1367 (CF), 1245, 1218, 1159, 969, 896, 880, 823 cm^{-1}; mp (**1a**) 40–41.5 °C; mp (**1b**) 51–53 °C.

Approximate rates of their quantitative isomerization to perfluorocyclooctatetraene were obtained by heating **1a** and **1b** in the gas phase in sealed Pyrex ampules immersed in an oil bath at 150 °C, with analysis by GLC: For **1a**, $t_{1/2} \approx 30$ min; for **1b**, $t_{1/2} = 3$–4 min.

***exo,cis*-7,8-Dibromo-*syn*-perfluorotricyclo[4.2.0.0^{2,5}]oct-3-ene (5).** To *syn*-tricyclooctadiene **1b** (57.6 mg, 0.23 mmol) in 0.5 mL of dry CCl_4 was added a solution of bromine (40.5 mg, 0.25 mmol) in 3 mL of the same solvent, and the mixture was stirred 2 h at room temperature. Most of the solvent was removed under reduced pressure, and the residual liquid was vacuum transferred into a −196 °C U-trap. Upon being warmed, the contents of the trap separated into solid and liquid phases. The latter was carefully vacuum transferred into a −78 °C storage bulb and then shown by IR spectroscopy to be mostly solvent. After being vacuum transferred to a sublimer, the solid portion was sublimed at 40 mm and 3.5 °C by using an ice–water condenser to give white crystals: mp 45–46 °C; IR (KBr) 1757 (FC=CF), 1376 cm^{-1} (CF); mass spectrum, *m/e* 408 (M$^+$), 222 (base).

***exo,cis*-7,8-Dibromo-*anti*-perfluorotricyclo[4.2.0.0^{2,5}]oct-3-ene (3).** *anti*-Tricyclooctadiene **1a** (1.32 g, 5.3 mmol) was dissolved in 10 mL of dry CCl_4 and cooled to ~10 °C. A solution of bromine (0.93 g, 5.8 mmol) in 1.5 mL of dry CCl_4 was added all at once, and the mixture was maintained at −28 °C for 21 h. NMR analysis indicated the product mixture to be ~80% the desired dibromide, ~10% the tetrabromide **4**, and ~10% unreacted diene **1a**. Solvent, excess bromine, and **1a** were removed carefully under reduced pressure, leaving a viscous liquid which was vacuum transferred into a U-trap at −78 °C. GLC analysis on a 9 ft × $^1/_4$ in., 10% QF-1 on Chromasorb W column at 110 °C and a flow rate of 160 mL/min revealed that this product (0.6 g) was ~95% pure dibromide. Analytically pure material was obtained by GLC trapping: IR (film) 1759 (CF=CF), 1368 cm^{-1} (CF); mass spectrum, *m/e* 408 (M$^+$), 222 (base).

Anal. Calcd for $C_8F_8Br_2$: C, 23.55; Br, 39.18. Found: C, 23.48; Br, 39.21.

***exo,cis*-3,4-*exo,cis*-7,8-Tetrabromo-*anti*-tricyclo[4.2.0.0^{2,5}]octane (4).** *anti*-Tricyclooctadiene **1a** (73 mg, 0.29 mmol) and bromine (50 μL, 0.87 mmol) were sealed in a Pyrex tube and allowed to stand for 3 h at room temperature. Excess bromine was removed under reduced pressure, leaving a solid residue which was sublimed at 45 °C (0.5 μm) to give colorless crystals (117 mg, 0.206 mmol, 72%). No attempt was made to improve this yield. A second sublimation yielded crystals with a melting point of 52–56 °C, and a third improved the melting point to 56.5–57.5 °C: IR (KBr) 1300, 1252, 1180, 1127, 1000, 965, 806 cm^{-1}.

Anal. Calcd for $C_8Br_4F_8$: C, 16.91; Br, 56.31. Found: C, 16.95; Br, 56.20.

***exo*- and *endo*-7-Chloro-*anti*-tricyclo[4.2.0.0^{2,5}]oct-3-enes (8 and 9).** A mixture of perfluorobenzene (75 g, 0.40 mol) and chlorotrifluoroethylene (11.5 g, 0.099 mol; both from Columbia Organic Chemicals) in a quartz tube was degassed by a single freeze–pump–thaw cycle and sealed. The tube was irradiated with the cylindrical photoreactor described above for 3 weeks, during which considerable polymer formed on the walls of the vessel. The product was fractionated by using a 9-in. Vigreux column, yielding unreacted perfluorobenzene (55.4 g, 0.30 mol) and a stereoisomeric mixture of bicyclic (**7**) and tricyclic (principally **8** and **9**) adducts boiling from 101 to ~110 °C (10.4 g, 0.034 mol, 34%): principal peaks in the mass spectrum of the adduct mixture *m/e* 302 (M$^+$), 283 (− F), 267 (− Cl), 252 (− CF_2), 248 (− CF), 233 (− CF_3), 217 (− CF_2Cl); IR (vapor) 1765 (FC=CF), 1359, 1305, 1184, 1158, 1041 cm^{-1}. Pure samples of **8** and **9** were obtained by GLC trapping on a 20 ft × $^1/_4$ in., 20% SF-96 on Chromasorb W AW DMCS column at 50 °C with a flow rate of 100 mL/min. Under these conditions the endo isomer **9** had a retention time of 18 min vs. 21 min for the exo olefin **8**.

Acknowledgment. The authors thank Howard S. Hutchins for guidance with the NMR measurements and both the National Science Foundation and the Petroleum Research Fund, administered by the American Chemical Society, for generous financial support.

Registry No. **1a**, 72777-10-7; **1b**, 74984-75-1; **3**, 74930-04-4; **4**, 74930-05-5; **5**, 74983-83-8; **7** (isomer 1), 74930-06-6; **7** (isomer 2), 74983-84-9; **8**, 74930-07-7; **9**, 74983-85-0; perfluorocyclooctatetraene, 57070-35-6; perfluorobenzene, 392-56-3; chlorotrifluoroethylene, 79-38-9.