1,2- and 1,8-Dichloroperfluorocyclooctatetraene: Stable Bond-Shift Isomers

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The title compounds **1** and **2** have been synthesized from hexafluorobenzene. Bond-shift interconversion of these isomers is slow even at 150 °C; kinetic and thermodynamic parameters for the isomerization have been evaluated. A study of **1** and **2** at high temperatures failed to reveal evidence for skeletal rearrangement. Both direct ultraviolet irradiation and triplet sensitization in solution effected rapid interconversion of these compounds; longer reaction times resulted in photocyclization to *anti*-tricyclo[4.2.0.0²,⁵]octa-3,7-dienes.

Bond-shift isomerization in cyclooctatetraene is very fast at ambient temperatures,[1] but it can be slow or nonexistent in multiply substituted derivatives of the molecule.[2,3] The title compounds, 1,2- and 1,8–dichloroperfluorocyclooctatetraene (**1** and **2**, respectively), appear to be the first pair of stable, isolated bond-shift isomers of a cyclooctatetraene bearing only single-atom substituents.[4] These molecules can be regarded as doubly labeled derivatives of perfluorocyclooctatetraene (**3**) in which the labels strongly resemble the atoms they


1   **2**   **3**
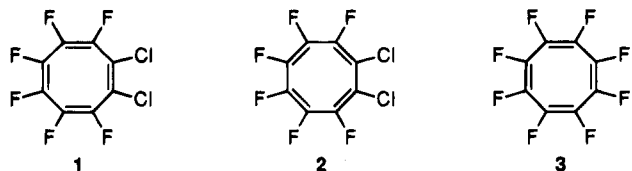
have replaced. As such, **1** and **2** are well suited in principle for studies designed to detect and mechanistically explore thermal and photochemical transformations of the perfluoro compound. Herein are described the synthesis of these bond-shift isomers, the kinetics and thermodynamics of their thermal interconversion, their behavior at high temperatures, and their photochemistry.

Results and Discussion

Synthesis. Trichloroethylene undergoes photocycloaddition to hexafluorobenzene to give bicyclic diene **4**, which photocyclizes under the reaction conditions to tricyclic olefin **5**.[5,6] Since the reaction is accompanied by the formation of a soft brown polymer which blocks access to the light source, a special apparatus was designed to minimize this problem (see Experimental Section). Utilizing a conventional photolysis assembly with a water-cooled immersion well, the apparatus continuously circulates the reactants through the photolysis vessel by

distillation and gravity flow. The two reactants and acetonitrile solvent all boil close to 85 °C; thus, they distill together and flow past the lamp while the far less volatile photoproducts collect in the distillation pot where they are protected from further irradiation.[7] Polymer buildup on the immersion well is much slower using this apparatus than is the case with a conventional setup.
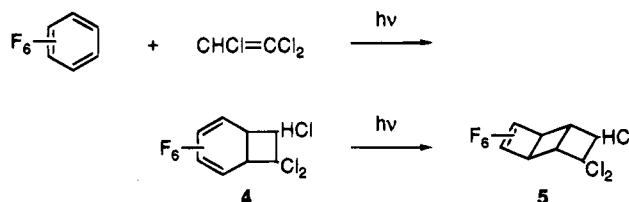
The product obtained in 70% yield by this method is a mixture of bicyclic and tricyclic adducts **4** and **5** because **4** is removed from the reaction zone before cyclization is complete and perhaps also because long heating in the distillation pot ring opens some of the **5** to **4**. In the present synthesis this is not a problem, as the next step is in fact that reaction. Heating the mixture under reflux (~170 °C) results in clean isomerization of the tricyclic to bicyclic product. Treatment of **4** with diazabicyclononane in acetonitrile at room temperature effects rapid dehydrohydrochlorination to **6** and disrotatory opening of the cyclohexadiene ring ensues immediately to give cyclooctatetraene **1**. Electrocyclic ring opening of **4** to its
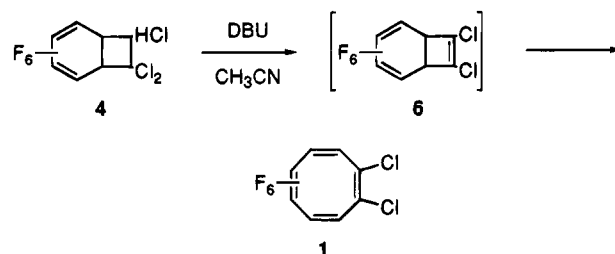
monocyclic isomer does not occur to a detectable extent at equilibrium, but in the case of **1** only the monocyclic form is observed. After low-temperature recrystallization and sublimation, white crystals of **1** melted at 35 °C; infrared stretching bands at 1695 and 1610 cm⁻¹ confirmed the presence of C—CF=CF—C and C—CCl=CCl—C

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(1) Naor, R.; Luz, Z. *J. Chem. Phys.* **1982**, *76*, 5662.
(2) Paquette, L. A. *Acc. Chem. Res.* **1993**, *26*, 57.
(3) Paquette, L. A. *Pure Appl. Chem.* **1982**, *54*, 987.
(4) One member of another such pair, 1,2,3,8-tetrachlorocyclooctatetraene, has been isolated and its bond-shift isomer has been both observed spectroscopically and trapped. Warrener, R. N.; Nunn, E. E.; Paddon-Row, M. N. *Tetrahedron Lett.* **1976**, 2355.
(5) For other cycloadditions of hexafluorobenzene to olefins, see Roberts, B. E.; Goldman, G. D.; Lemal, D. M. *J. Fluorine Chem.* **1990**, *48*, 353; and refs therein.
(6) Takenaka, N. E.; Lemal, D. M. In *Synthetic Fluorine Chemistry*; Chambers, R. D., Olah, G. A., Prakash, S., Eds.; Wiley: New York, 1992; pp 287–312.

(7) A nitrogen atmosphere appears to inhibit the reaction. Perhaps oxygen assists it by functioning as a triplet quencher, for we have shown that diene **4** fragments into the starting materials when excited to its triplet state (ref 5).

structural units, respectively. The ^{19}F NMR spectrum (CDCl$_3$) displayed multiplets at -112.6 (F$_3$, F$_8$), and -126.1 ppm (F$_4$–F$_7$); cf. **3**, -123.1 ppm.

Some attention to the stereochemical aspects of the synthesis described above is appropriate. When the photocycloadditon is carried out under static conditons with monitoring by ^{19}F NMR, signals for a single bicyclic stereoisomer can be detected as those of a single tricyclic isomer develop. Thermal ring opening of the tricyclic olefin yields a 4:1 equilibrium mixture of bicyclic stereoisomers in which the previously observed isomer predominates. We assign this stereoisomer (**4a**) the exo-H configuration and the minor form (**4b**) the endo-H configuration by analogy to **7** and **8**. Only **7** is detected in the equilibrium mixture of these dienes, presumably because dipole–dipole repulsion is considerably smaller when the chlorines are endo.[6,8] Since the stereoisomer of **4** observed as an intermediate during the photoreaction (**4a**) has the exo-H configuration, the single tricyclic isomer **5** must also, as shown below. Photocyclization of
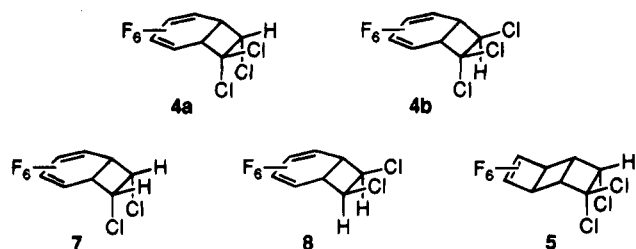
4a could of course yield a syn as well as an anti skeleton, but in all of the photocyclizations (more than a dozen) of highly fluorinated bicyclo[4.2.0]octa-2,4–dienes we have examined, anti isomers are formed.[5,6,8]

When a sample of **1** was heated in an ampule at 275 °C, the product was a clean ~1:2 mixture of the starting material and a new compound of slightly shorter GC retention time but identical mass spectrum. Its IR and ^{19}F NMR spectra confirmed that the new colorless liquid was 1,8-dichloroperfluorocyclooctatetraene (**2**), the bond-shift isomer of **1**. Double bond stretching bands at 1705 and 1650 cm^{-1} (neat) revealed the presence of C–CF=CF–C and C–CF=CCl–C units, respectively. The latter band lies halfway between the 1695 and 1610 cm^{-1} bands of **1**, consistent with double bonds which are "hybrids" of those in **1**. This structural feature was also revealed by a low field ^{19}F NMR signal (CDCl$_3$) at -97.0 ppm (F$_2$, F$_7$); others of equal area appeared at -123.7 (F$_3$, F$_6$) and -124.8 ppm (F$_4$, F$_5$).

Kinetics and Thermodynamics of the Bond-Shift Isomerization. Solutions of **1** in 1,2,4-trichlorobenzene were heated in a constant temperature bath at four temperatures in the 135–180 °C range, and the ratio of **1** to **2** as a function of time was measured by ^{19}F NMR. The resulting macroscopic rate constants are given in Table 1, together with values of the equilibrium constant. At 150 °C, for example, the half-life for approach to equilibrium was 62 min. *Thus, these cyclooctatetraenes are stoutly resistant to bond-shift isomerization.*

A van't Hoff plot of the equilibrium data gave $\Delta H° = -0.7 \pm 0.2$ kcal/mol and $\Delta S° = 0.0 \pm 0.5$ eu. Eyring plots for the forward and reverse reactions yielded activation parameter values which are presented in Table 2, together with values for heptafluorocyclooctatetraene[9] and

Table 1. Rate and Equilibrium Constants for Interconversion of Cyclooctatetraenes 1 and 2

T (°C)	k (s^{-1})^a	$K_{2/1}$
135.0	$4.97 \pm 0.68 \times 10^{-5}$	2.31
150.1	$1.86 \pm 0.21 \times 10^{-4}$	2.22
165.2	$6.38 \pm 0.33 \times 10^{-4}$	2.17
180.2	$2.04 \pm 0.23 \times 10^{-3}$	2.13

^{a} These are the macroscopic rate constants. Errors are 95% confidence limits.

Table 2. Activation Parameter Values for Cyclooctatetraene Bond-Shift Isomerizations

cyclooctatetraene	T (°C)	$\Delta G^{\ddagger}$ (kcal/mol)	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (eu)
1^a	165.2	32.7 ± 0.1	29.2 ± 0.7	-7.2 ± 0.8
2^a	165.2	33.4 ± 0.1	29.9 ± 0.5	-7.2 ± 0.6
heptafluoro^b	116	24.6 ± 0.1	21.1 ± 0.9	-10.2 ± 2.5
unsubstituted^c	0	13.0	10.0	-9.7

^{a} Errors are 95% confidence limits. ^{b} Reference 9. ^{c} Reference 1. These activation quantities were calculated from values of $1/\tau$, which are twice the unidirectional rate constant. The measurements were made in a liquid crystal solvent.

the parent hydrocarbon.[1] The doubling of the activation enthalpy for bond-shift isomerization which accompanies substitution of seven fluorines for hydrogen in cyclooctatetraene has been ascribed principally to nonbonded repulsion in the transition state (dipole–dipole repulsion contributing surprisingly little). Seemingly modest, the further increase in steric bulk upon substitution of chlorines for a hydrogen and fluorine in the heptafluoro derivative has resulted in another marked increase in $\Delta H^{\ddagger}$. Though no single substituent on the ring is large, the cumulative buttressing effect of eight atoms larger than hydrogen suffices to roughly triple the bond-shift barrier height for cyclooctatetraene.[10] Activation entropies for all of these processes are substantially negative.

The detailed pathway of the bond-shift isomerization in cyclooctatetraenes has been the focus of much effort and controversy.[2] Hrovat and Borden have recently argued on the basis of high level ab initio calculations that for the parent hydrocarbon the transition state is flat, having D_{8h} symmetry.[11] Paquette strongly espouses a nonplanar alternative, a "flattened saddle geometry", for sterically congested and geometrically constrained derivatives of cyclooctatetraene which his group has studied.[2,12] Steric hindrance to bond-shift isomerization in **1** and **2** is sufficiently severe that a nonplanar transition state seems highly likely.

Search for Thermal Skeletal Rearrangement. The availability of thermally stable, doubly labeled derivatives **1** and **2** of perfluorocyclooctatetraene **3** made it possible for us to explore the question whether skeletal

(8) Rahman, M. M.; Secor, B. A.; Morgan, K. M.; Shafer, P. R.; Lemal, D. M. *J. Am. Chem. Soc.* **1990**, *112*, 5986.

(9) Spector, T.; Rahman, M. M.; Shafer, P. R; Lemal, D. M., manuscript in preparation.

(10) The role of buttressing is apparent in a comparison of the ease of bond-shift isomerization in 1,2,5,6- versus 1,2,3,4-tetramethylcyclooctatetraene. Whereas the former equilibrates with its isomer at room temperature, the latter undergoes this transformation in refluxing diglyme (162 °C). Paquette, L. A.; Photis, J. M. *J. Am. Chem. Soc.* **1976**, *98*, 4936. Paquette, L. A.; Photis, J. M.; Ewing, G. D. *J. Am. Chem. Soc.* **1975**, *97*, 3538.

(11) Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1992**, *114*, 5879.

(12) By analogy to his conclusion that bond-shift isomerization in cyclobutadiene proceeds via heavy-atom tunneling, Carpenter suggested that the same process may contribute to bond-shifting in cyclooctatetraene. He cited the relatively large negative entropy of activation in support of this surmise (Carpenter, B. K. *J. Am. Chem. Soc.* **1983**, *105*, 1700). Calculations by Dewar gave further credence to Carpenter's idea (Dewar, M. J. S.; Merz, K. M., Jr. *J. Phys. Chem.* **1985**, *89*, 4739).

rearrangement occurs at elevated temperatures in highly fluorinated cyclooctatetraenes. Paquette has demonstrated that at temperatures ≥400 °C in a flow system scrambling of the skeletal atoms takes place in a variety of cyclooctatetraene derivatives.[13] His group has shown that the scrambling occurs via bicyclo[4.2.0]octatriene valence isomers, which undergo internal Diels−Alder/retro-Diels−Alder reactions and/or [1,5] sigmatropic rearrangements of carbon. For derivatives of **3** another mechanism, criss-cross [2 + 2] cycloaddition/[2 + 2] cycloelimination, might supervene in light of the rather facile thermal cyclization of highly fluorinated 1,5-cyclooctadienes to tricyclo[3.3.0.0^{2,6}]octanes, e.g. **9** → **10**.[14,15] We hoped to distinguish among these possibilities by finding a scrambling pattern for the chlorine labels on the cyclooctatetraene skeleton.
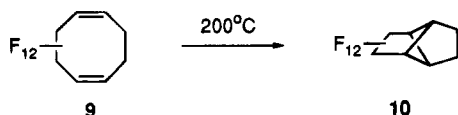
Skeletal rearrangement of **1** was attempted by both static and flow pyrolysis methods. Flow pyrolyses were carried out in both Pyrex and quartz tubes at different pressures in the range 350−500 °C. Under conditions vigorous enough to alter starting material, the reaction product was very complex and was not resolved into its components. Heating **1** in silated Pyrex ampules also yielded ill-defined decomposition products, but gave in addition, in about 25% crude yield, a dimer which was purified by kugelrohr distillation and eventually obtained as white crystals, mp 121 °C. The compound has 2-fold symmetry, as revealed by six signals of equal area in its ^{19}F NMR spectrum. These and other spectral data on the dimer are presented in the Experimental Section, but its structure remains unknown. Crystals submitted for X-ray analysis were found to be disordered.

We conclude that **1** and **2**, stable as they are, are insufficiently robust to serve as models for and probes of skeletal rearrangement in the perfluorotetraene **3**. At the high temperatures required for this study, carbon−chlorine bond strengths are probably the limiting factor.[16] In **11**, for example, which undoubtedly exists in equilibrium with **2** at elevated temperatures, the bridgehead
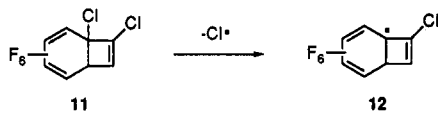
C−Cl bond is strongly activated for homolysis to give **12** (or heterolysis to yield a carbocation, especially if a trace of acid is present[17]) by the unsaturation flanking it on both sides. Since **3** itself can be recovered unchanged even after brief heating at 500 °C, it is likely that undetectable degenerate skeletal rearrangement does occur in this molecule under conditions it can survive. The answer to the questions whether and how this

transpires must await experiments with **3** itself, doubly labeled with ^{13}C.

Photochemistry. Irradiation of tetraene **1** resulted in very efficient photoequilibration with **2**, even at low temperatures.[3,4,18] The photostationary state composition rapidly achieved with a Vycor-filtered medium-pressure mercury arc in acetonitrile at 15 °C was about 1:1.5 (**1** to **2**). When **1** was triplet sensitized with acetophenone, the same isomer ratio was obtained. This agreement
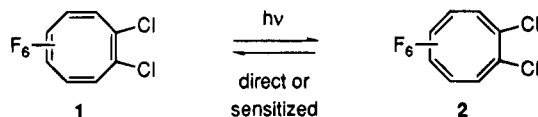
suggests that, even when **1** or **2** is initially excited into a singlet state, bond-shift isomerization occurs in the lower-lying T_1 state or (less likely) in the vibrationally hot ground state. By analogy to these model compounds, it is a good surmise that **3** suffers degenerate bond-shift rearrangement upon irradiation.

On continued irradiation, the photostationary mixture of **1** and **2** gave rise to two new compounds. Though neither was isolated, analysis of their ^{19}F NMR spectra with the help of spin decoupling and comparison with the spectra of several closely related tricyclooctadienes[6,19,20] leaves no doubt about their structures. The more abundant of the two is 3,4-dichloroperfluorotricyclo[4.2.0.0^{2,5}]octa-3,7-diene (**13**), with three resonances of equal area at −118.6 (d, F_A's), −178.1 (d, F_B's), and −185.4 ppm (q, F_C's). Apparent coupling constants are $J_{AB} = 0$; $J_{AC} = 7.(7)$; $J_{BC} = 17.(6)$ Hz. The other photoproduct is 2,3-
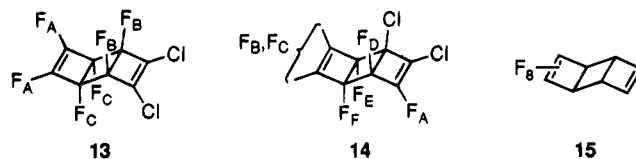
dichloroperfluorotricyclo[4.2.0.0^{2,5}]octa-3,7-diene (**14**), which gave signals at −102.4 (F_A), −119.6 to −119.9 (F_B, F_C), −175.7 (F_D), −176.4 (F_E), and −185.6 ppm (F_F). Formation of these tricyclooctadienes, which presumably takes place via bicyclo[4.2.0]octatriene valence isomers, parallels the photocyclization of perfluorotetraene **3** to tricyclic diene **15**.[20,21] This photochemical behavior contrasts sharply, however, with that of cyclooctatetraene itself and most of its derivatives.[22]

Conclusion. The vigorous conditions required to interconvert isomers **1** and **2** thermally show that the cumulative effect of small substituents on a cyclooctatet-

(13) Paquette, L. A.; Oku, M.; Heyd, W. E.; Meisinger, R. H. *J. Am. Chem. Soc.* **1974**, *96*, 5815.

(14) Prober, M.; Miller, Jr., W. T. *J. Am. Chem. Soc.* **1949**, *71*, 596. Karle, I. L.; Broge, R. W. *J. Am. Chem. Soc.* **1964**, *86*, 2523.

(15) Highly fluorinated tricyclo[4.2.0.0.^{2,5}]octanes also rearrange thermally to tricyclo[3.3.0.0.^{2,6}]octanes, presumably via 1,5-cyclooctadienes. Steffen, M.; Saunders, W. D.; Lemal, D. M., unpublished work.

(16) For a carbon bearing a single fluorine, the C−F bond is roughly 25 kcal/mol stronger than the corresponding C−Cl bond. McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493.

(17) In a beautiful study by Huisgen, the thermal rearrangement of bromocyclooctatetraene to *trans-β*−bromostyrene was shown to proceed via ionic cleavage of the C−Br bond in 1-bromobicyclo[4.2.0]-octa-2,4,7-triene. Huisgen, R.; Konz, W. E. *J. Am. Chem. Soc.* **1970**, *92*, 4102. Konz, W. E.; Hechtl, W.; Huisgen, R. *J. Am. Chem. Soc.* **1970**, *92*, 4104.

(18) Light-induced bond-shift isomerization has been observed with other cyclooctatetraenes. Anet, F. A. L.; Bock, L. A. *J. Am. Chem. Soc.* **1968**, *90*, 7130); and refs 3, 4.

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

(20) Barefoot, A. C., III; Saunders, W. D.; Buzby, J. M.; Grayston, M. W.; Lemal, D. M. *J. Org. Chem.* **1980**, *45*, 4292.

(21) A preliminary study of the temperature dependence for photocyclization of **3** reveals that formation of the bicyclic intermediate is probably a thermal process. That intermediate has been shown to photocyclize even at 20 K (Waldron, R. F.; Barefoot, A. C., III; Lemal, D. M. *J. Am. Chem. Soc.* **1984**, *106*, 8301).

(22) Hassenruck, K.; Martin, H-D.; Walsh, R. *Chem. Rev.* **1989**, *89*, 1125. Fray, G. I.; Saxton, R. G. *The Chemistry of Cyclooctatetraene and its Derivatives*; Cambridge University Press: Cambridge, 1978.
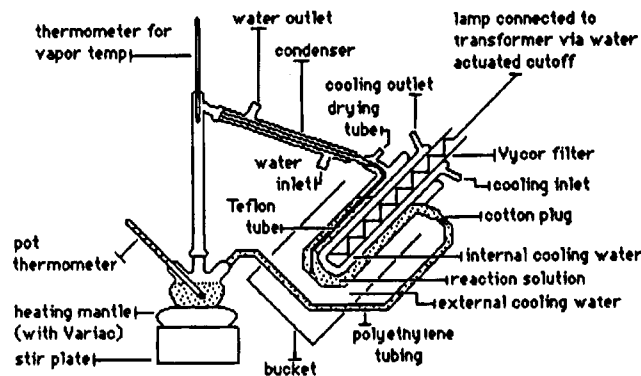
Figure 1. Recycling flow photolysis apparatus.

raene can generate a high barrier to bond-shift isomerization. Though a high temperature search for skeletal rearrangement in these doubly labeled derivatives of fluorocarbon **3** was unrewarding, the labels revealed another process which had been invisible in **3**: facile photochemical bond-shift isomerization. A slower photoreaction yielded tricyclooctadienes.

Experimental Section

^{19}F NMR spectra were measured at 56.2 MHz on a JEOL FX-60Q FT spectrometer or at 282.2 MHz on a Varian XL 300 spectrometer in CDCl$_3$ with chemical shifts reported in ppm from internal CFCl$_3$ (Φ scale, upfield negative). Mass spectra were measured on a Finnigan 4023 quadrupole mass spectrometer, except for the low and high resolution spectra of the dimer. These were determined at the Midwest Center for Mass Spectrometry at the University of Nebraska in Lincoln. UV spectra were taken on a Hewlett-Packard diode array spectrometer, and IR spectra were determined on a Perkin-Elmer 599 spectrophotometer (KBr for solids, neat for liquids). Analytical gas chromatograms were obtained using a Hewlett-Packard 5880A gas chromatograph (25 m methylsilicone capillary column) with flame ionization detector. Preparative gas chromatographic work was performed on a Hewlett-Packard 5750 gas chromatograph equipped with a 25 ft x $^1/_4$ in. 20% QF-1-on-Chromasorb-W-HP column and thermal conductivity detector. Melting points were determined on a Thomas-Hoover Uni-Melt capillary melting point apparatus in open capillary tubes and are uncorrected. Kinetic measurements were made using a Haake F3 constant temperature bath which controlled temperatures to ±0.1 °C. Elemental analyses were performed by Spang Microanalytical Laboratory, Eagle Harbor, MI. The photolysis apparatus was a Canrad-Hanovia 450 W medium pressure mercury lamp surrounded by a Vycor filter and contained in a water-cooled quartz well.

Pyrex pyrolysis tubes were silated by the addition of a small amount of N,O-bis(trimethylsilyl)acetamide and heating to reflux over a flame (hood), allowing the liquid to make contact with the entire inner surface of the ampule. The tubes were then cooled, rinsed with acetone and dried in an oven at 200 °C. Hexafluorobenzene was obtained from Fairfield Chemical Co., and other chemicals from Aldrich Chemical Co.

1,2-Dichloroperfluorocyclooctatetraene (1). A photolysis apparatus incorporating a distillation setup was assembled in such a way that the distillate (solvent and starting materials) flowed by gravity into a cylindrical photolysis vessel surrounding the quartz lamp well and then returned to the distillation pot (Figure 1). The distillation setup comprised a 500 mL three-necked flask heated with a mantle and fitted with an elongated distillation head which was connected through a water condenser to the photolysis vessel. A length of narrow Teflon tubing delivered the distillate to the bottom of the vessel, and an outlet at the top carried effluent via a cotton plug through a polyethylene tube back to the distillation pot. The photolysis vessel, which was vented to the atmo-

sphere through a drying tube, was immersed in a bucket through which cold water was passed to supplement the cooling provided by the quartz well.

A solution of acetonitrile (200 mL, bp 82 °C), trichloroethylene (35 mL, 51 g, 0.39 mol, bp 88 °C), and hexafluorobenzene (20.5 mL, 33 g, 0.18 mol, bp 82 °C) was apportioned between the distillation flask and the photolysis vessel. The flask was heated to initiate distillation and the irradiation was begun. The reaction mixture became dark brown, and polymer buildup on the quartz well required its removal daily for cleaning with acetone and detergent. Photolysis was terminated after several days, when little hexafluorobenzene remained. Solvent and reactants were removed by distillation at atmospheric pressure, and the residue was distilled through a short Vigreux column. The colorless liquid product, collected at ~75 °C and 10 torr, was a mixture of 7H-7,8,8-trichloroperfluorobicyclo-[4.2.0]octa-2,4–diene (**4**) and 7H-7,8,8-trichloroperfluorotricyclo-[4.2.0.0^{2,5}]oct-3-ene (**5**) (34 g, 61%). The tricyclic olefin displayed narrow multiplets at −118.5, −119.6 (vinyl F's); −156.2, −157.3 (bridgehead F's proximal to Cl); −186.7, −188.4 ppm (remaining bridgehead F's).

To a 50 mL boiling flask was added 15.0 g of this mixture, and the neat liquid was refluxed (~170 °C) under nitrogen with magnetic stirring for 18 h. ^{19}F NMR analysis of the resulting clear tan liquid showed no peaks for the tricyclic olefin, but signals for both the exo-H and endo-H isomers of **4** (ratio 4:1). Exo-H: −149.7 to ~ −153 (m, 5F), −172.5 ppm (s, 1F); endo-H: −147.8 (s, 1F), ~-150 (4F), −189.3 ppm (m, 1F). Distillation of the tan liquid (70–80 °C, 15 torr) gave 13.1 g (87% yield) of colorless diene **4**.

To a 250 mL boiling flask was introduced diene **4** (10.0 g, 31.5 mmol) and acetonitrile (100 mL). During a 5-min period, diazabicyclononane (4.30 g, 34.6 mmol, 10% excess) was added dropwise with stirring. Reaction was immediate, giving a clear brown solution. After 5 h the reaction mixture was poured into 10% HCl (200 mL), and the heavy brown oil which separated was removed by extraction with pentane (3 × 50 mL). The combined pentane layers were back-extracted with water (2 × 100 mL) to remove acetonitrile and then dried (Na$_2$SO$_4$) and stripped on a rotary evaporator at room temperature. The remaining purple liquid was distilled at 70 °C and 10 torr, and a heat gun was used to assist the flow of the colorless, viscous tetraene to the receiver. Liquid at room temperature, the product crystallized in a freezer (6.29 g, 71%). The tetraene was recrystallized from a minimum of isopentane at −78 °C, and solvent was removed at this temperature. Sublimation at 33–34 °C and 10 torr gave crystals with mp 35 °C (sharp). IR (KBr): 1695, 1610, 1345, 1300, 1255, 995, 855, 795 cm^{-1}. MS m/e: 280 (M$^+$); 245 (M$^+$ − Cl), 226 (M$^+$ − Cl,F); 210 (M$^+$ − 2Cl). Anal. Calcd for C$_8$F$_6$Cl$_2$: C, 34.19%; Cl, 25.23%; F, 40.57%. Found: C, 33.97%; Cl, 25.28%; F, 40.45%.

1,8-Dichloroperfluorocyclooctatetraene (2). A heavy-walled Pyrex ampule (10 x 0.8 cm) was silated, filled with tetraene **1** (170 mg, 0.60 mmol) and sealed under vacuum after degassing with three freeze-pump-thaw cycles. The ampule was heated at 275 °C for 4 h, then cooled, and opened. ^{19}F NMR showed the product to be a ~1:2 mixture of **1** and its bond-shift isomer **2**, free of contaminants. Tetraene **2** was obtained pure as a colorless liquid by preparative gas chromatography (inj 185 °C, oven 140–155 °C at 1 °C/min). IR (neat): 1770, 1705, 1650, 1370, 1330, 1220, 1150, 1030, 940, 860, 810 cm^{-1}. MS m/e: 280 (M$^+$), 245 (M$^+$ − Cl, base), 226 (M$^+$ − F,Cl), 210 (M$^+$ − 2Cl). Anal. Calcd for C$_8$F$_6$Cl$_2$: C, 34.19%; Cl, 25.23%; F, 40.57%. Found: C, 34.25%; Cl, 25.40%; F, 40.41%.

Bond-Shift Isomerization Kinetics. A solution of dichloroperfluorocyclooctatetraene (**1**) (240 mg) in freshly distilled 1,2,4–trichlorobenzene (6.00 g, ~4 mL) was partitioned equally among eight thin-walled NMR tubes. The tubes were carefully degassed, sealed *in vacuo*, and stored in a freezer until used. Tubes were fully immersed in the constant temperature bath (two per run) for specified time periods, removed, and rapidly cooled with cold water. Isomer ratios were determined by integration of the well-isolated lowest field signals of each; integrations on the two tubes generally agreed to within 1%. The tubes were then immersed again to obtain the values for

the next point. Infinity values were obtained after at least 8 half-lives and were confirmed by further heating. Runs were performed at 135.0, 150.1, 165.2, and 180.2 °C.

The macroscopic rate constant for each run was given by the slope of a plot of $\ln[(1 - f_\infty)/(f - f_\infty)]$ versus time, where f is the fraction of starting material at a given time and f is the fraction remaining at equilibrium. The microscopic rate constants were obtained from the relations $k_{1\rightarrow2} = k/(r_\infty + 1)$ and $k_{2\rightarrow1} = r_\infty \cdot k_{1\rightarrow2}$, where r_∞ is the equilibrium ratio of **1** to **2**.

High Temperature Pyrolysis of Tetraene 1. Static Pyrolysis. Tetraene **1** (50 mg) was placed in a silated Pyrex ampule (10 × 0.8 cm), which was degassed, sealed *in vacuo,* and heated at 300 °C. The heating device was a vertically mounted iron pipe wrapped with heating tape; temperature was controlled with an Omega Model 149 controller and monitored with a thermocouple attached to the ampule. After 8 h the ampule was opened to give a brown oil whose ^{19}F NMR spectrum revealed, in addition to many smaller peaks, six signals of approximately equal area. This liquid was distilled in a kugelrohr to give a yellow oil collected at 65 °C and 0.2 torr. After a week in a freezer (−25 °C) the oil had deposited large, clear crystals which were wiped clean on filter paper and sublimed at 60 °C and 0.1 torr. The resulting small white crystals melted at 120.5−121.5 °C, and resublimation gave crystals melting sharply at 121 °C. Variable from run to run, the NMR yield averaged ˜25%; the yield of pure material was ~5%. ^{19}F NMR: −117.9 (subsplit t), −139.1 (m), −139.5 (m), −146.2 (m), −161.2 (s), and −191.8 ppm (s); all areas equal. Decoupling experiments showed that the first signal was coupled to the second and fourth, the second to the fourth, and the third to the sixth. IR (KBr): 1746, 1664, 1360, 1280, 1220, 1000, 940, 830, 760 cm^{-1}. MS *m/e*: 560 (M$^+$), 525 (M$^+$-Cl), 245 (C$_8$F$_6$Cl$^+$), 210 (C$_8$F$_6$$^+$). Exact mass determination on parent cluster: 559.8566 (theor. 559.8562), 561.8535 (theor. 561.8534), 563.8506 (theor. 563.8507). UV (isooctane): λ max 222 nm (ϵ 10 000).

Flow Pyrolysis. Tetraene **1** (50 mg) was placed in a 5 mL round-bottom flask which was then attached to a Pyrex or quartz pyrolysis tube (50 × 0.8 cm) surrounded by another Pyrex tube encased in heating tape. The temperature of the pyrolysis tube was controlled by an Omega Model 149 controller and monitored by thermocouples located in the annular space between the tubes and in the heating tape. Effluent from the pyrolysis tube passed through a U-trap cooled in liquid nitrogen and conected to a vacuum pump. Pyrolyses were carried out under a variety of conditions: Pyrex tube, 350−500 °C at 0.3 torr in 25 °C increments; Pyrex, 425 °C at 5 and 10 torr; quartz, 400 and 425 °C at 0.3 torr. The sample tube was cleaned with acetone and evacuated between runs. The ^{19}F NMR spectrum of the clear yellow liquid pyrolysate from runs producing other than starting material was very complicated, showing several dozen large and many small signals in the range −90 to −140 ppm.

Photoisomerization of Tetraene 1. The photolysis apparatus was a Canrad-Hanovia 450 W medium pressure mercury lamp surrounded by a Vycor filter and contained in a water-cooled quartz jacket. To a 5 mm quartz NMR tube was added a solution of tetraene **1** (20 mg) in acetonitrile (˜1 mL). Oxygen was expelled from the sample by bubbling nitrogen through it for several minutes, and then the tube was capped and sealed with Parafilm. It was strapped to the quartz jacket, and the whole assembly was immersed in a water bath maintained at 15 °C by a constant flow of tap water. After 1 h of irradiation, a stationary state had been reached in which the ratio of **1** to **2** was 1:1.5. By 3.5 h small signals for **13** had appeared, and by 10.5 h peaks for **14** had grown out of the base line. The ratio of **1** to **2** remained at 1:1.5. The two tricyclic compounds now comprised roughly 18% of the mixture, and the ratio of **13** to **14** was ~1.6:1. Photolysis of **1** was also carried out in similar fashion at −30 °C, with the sample tube suspended in a tubular quartz dewar through which a constant stream of cold nitrogen was passed. Again the photostationary state mixture of bond-shift isomers was reached within 1 h.