The Perfluoro-1,3,5-hexatrienes[1]

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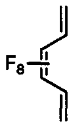
trans-Perfluoro-1,3,5-hexatriene was obtained by catalytic isomerization of the cis isomer, and their configurations were confirmed by a photochemical method. Equilibration of these isomers with iodine and light at 13 °C revealed that the cis isomer is slightly more stable than the trans ($K_{c\rightarrow t} = 0.83$). The trienes undergo reactions under the influence of heat and light which contrast with those of their hydrocarbon counterparts. Cis triene cyclizes reversibly to perfluoro-3-vinylcyclobutene at 160 °C ($K_{eq} = 12.2$), and at higher temperatures perfluoro-1,3-cyclohexadiene is formed irreversibly. Cyclization of trans triene to the vinylcyclobutene is much slower than that of the cis isomer, as required by the finding that thermal ring opening of the vinylcyclobutene gives cis triene cleanly. Ultraviolet irradiation of the trienes with and without mercury sensitization yields the same two cyclization products, but the cyclohexadiene undergoes a further rapid photocyclization to give perfluorobicyclo[2.2.0]hex-2-ene, as reported recently by Dedek's group. Mercury photosensitization of the vinylcyclobutene proceeds smoothly to yield this same bicyclic olefin.

The thermal and photochemistry of 1,3,5-hexatrienes have been extensively investigated.[2,3] In addition to its relationship to vitamin D, this chemistry played an important role in the development of the theory of concerted reactions.[4-6] At the outset of the present work, however, only a single isomer of the fully fluorinated parent 1,3,5-hexatriene was known.[7] Its configuration was not known, and its chemistry was almost entirely unexplored. As the simplest perfluoropolyenes, *cis*-and *trans*-perfluoro-1,3,5-hexatriene (**1** and **2**, respectively)occupy a position of significance in fluorocarbon chemistry. We therefore determined their configurations, equilibrated them, and studied their thermal and photochemistry. Just before submission of a paper on this work, a report appeared from Dedek's laboratory describing several of the same results we had obtained.[8] This paper therefore focuses on that portion of our investigation which complements the work of the Czech researchers.



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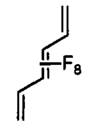

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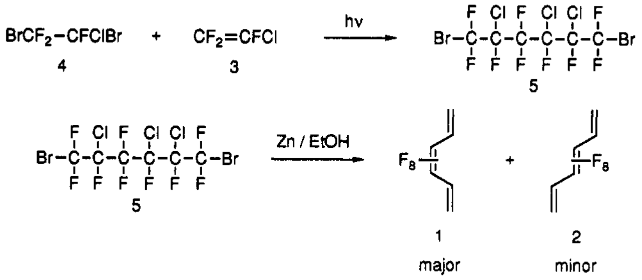
Results and Discussion

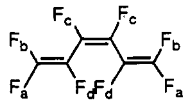
Synthesis and Properties. The trienes were synthesized from chlorotrifluoroethylene (**3**) by the method of Dědek and Chvátal (Scheme 1).[7] Photolysis of the dibromide (**4**) derived from **3** in the presence of more **3** gave a mixture containing the radical coupling product **5**. Dechlorination of **5** with zinc gave perfluoro-1,3,5-hexatriene in 66% yield. A single isomer had been reported, but gas chromatographic analysis revealed the presence of the other isomer too, as 10–15% of the total triene.

Scheme 1



Surprisingly, the major isomer proved to have the cis configuration, as is discussed later in this paper. In the zinc reduction, the two terminal double bonds are introduced first, as indicated by the fact that a great deal of 3-chloro-1,5-diene is found if the reaction is not taken to completion. Attack on the final chlorine very likely yields an allylzinc intermediate. Perhaps the odd stereoselectivity in the reduction stems from complexation of the isolated π bond in this intermediate with the metal; fluoride elimination from such a complex would give the cis triene.

cis-Perfluoro-1,3,5-hexatriene gave a ^{19}F NMR spectrum ($CDCl_3$) with resonances at −90.2 (m, F_a), −105.6 (dm, J = 115 Hz, F_b), −133.7 (m, F_c), and −181.8 ppm (dt, J = 115, 30 Hz, F_d). The spectrum of the trans isomer ($CDCl_3$) had signals at −91.2 (m, F_a), −104.4 (dm, J = 115 Hz, F_b), −150.8 (m, F_c), and −185.0 (dm, J = 115 Hz, F_d). The maxima for the two trienes in the near-ultraviolet are blue-shifted relative to those of the corresponding hydrocarbons[9] and extinction coefficients are lower in the fluorocarbons, but in both pairs the trans isomer absorbs more intensely:



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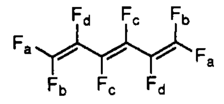

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• Abstract published in *Advance ACS Abstracts*, March 15, 1994.

[1] This work was reported at the Eleventh Winter Fluorine Conference, St. Petersburg Beach, FL, Jan 1993.

[2] de Kock, R. J.; Mennaard, N. G.; Havinga, E. *Rec. Trav. Chim.* **1960**, *79*, 922.

[3] Srinivasan, R. *J. Am. Chem. Soc.* **1960**, *82*, 5063; **1961**, *83*, 2806.

[4] Havinga, E.; de Kock, R. J.; Rappold, M. P. *Tetrahedron* **1960**, *11*, 276.

[5] Woodward, R. B.; Hoffmann, R. *J. Am. Chem. Soc.* **1965**, *87*, 395.

[6] Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Verlag Chemie: Weinheim, 1970; pp 51–3 and references cited therein.

[7] Dědek, V.; Chvátal, Z. *J. Fluorine Chem.* **1986**, *31*, 363.

[8] Hrabal, R.; Chvátal, Z.; Dědek, V. *J. Fluorine Chem.* **1993**, *63*, 185.

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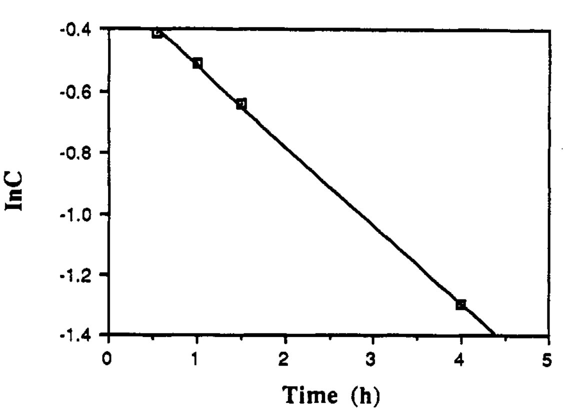
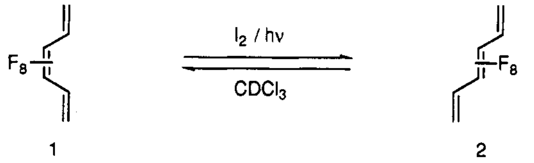


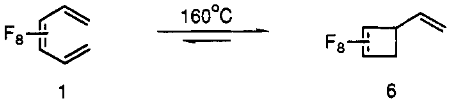
Figure 1. Equilibration of *cis*-perfluoro-1,3,5-hexatriene (1) with perfluoro-3-vinylcyclobutene (6). Plot of ln [1] versus time at 160 °C (σ^2 = 1.000).

cis-1, λ_{max} (c-C_6H_{12}) 236 nm (ϵ 8700; λ_{sh} 210 nm) vs λ_{max} 252 nm (ϵ 14 000);[10] *trans*-2, λ_{max} (c-C_6H_{12}) 242 nm (ϵ 12 500) vs λ_{max} 251 nm (ϵ 21 000).[10] While the electronic spectra of the hydrocarbons have very well developed vibrational fine structure, this is entirely missing in the fluorocarbon spectra.[11]

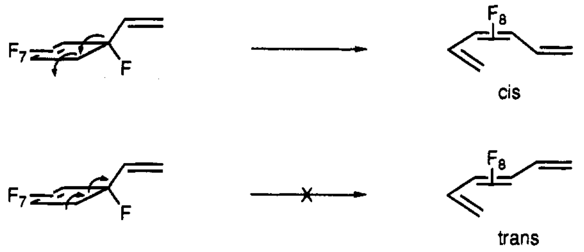
Irradiated with a sunlamp, iodine rapidly equilibrated the cis and trans trienes. At 13 °C in $CDCl_3$, $K_{c\rightarrow t}$ = 0.83. It may seem surprising at first that the two isomers are so close in free energy, with the cis actually the stabler form. Since even perfluoro-1,3-butadiene prefers a cis-skew conformation (dihedral angle ~47°) for steric reasons,[12-14] F–F nonbonded repulsions presumably prevent planarity in both triene isomers; both probably exist in skew–skew conformations. If, as a result, conjugation energy is small in *both* forms, their nearly identical free energy content is not so surprising.



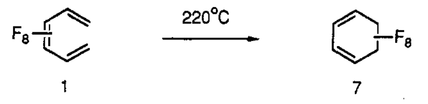
Thermal Chemistry. When the parent *cis*-1,3,5-hexatriene is heated at ~160 °C, it cyclizes to 1,3-cyclohexadiene; subsequent disproportionation of the diene to cyclohexene and benzene is slow at this temperature but becomes important at somewhat higher temperatures.[15] The fluorocarbon triene behaves entirely differently. At 160 °C 1 cyclizes reversibly to 3-vinylcyclobutene 6; the half-life for approach to equilibrium is 2.66 h, and K_{eq} = 12.2 (Figure 1). This value for the equilibrium constant was confirmed by starting the equilibration with pure vinylcyclobutene. Since no trans triene 2 was observed even after long equilibration times (>20 h), ring opening of the cyclobutene is highly stereoselective. As required by this result, we found that cyclization of 2 to 6 is far slower than that of 1.



Orbital-topology-allowed conrotatory ring opening could yield either 1 or 2, and steric considerations clearly favor the transition state leading to 2. However, inward rotation of the trifluorovinyl group in preference to the fluorine at the 3-position is consistent with the discovery of Burton and Dolbier that fluorine substituents at the 3- and 4-positions have a very powerful tendency to rotate outward in cyclobutene ring openings.[16,17] As calculations by Rondan and Houk have revealed, π donor substituents such as fluorine prefer outward rotation both to maximize a stabilizing interaction with the LUMO and to minimize a destabilizing one with the HOMO in the transition state for electrocyclic opening of cyclobutenes.[18,19] Apparently, the trifluorovinyl group is not as effective as fluorine in functioning as a π donor in one or both of these transition states.



Increasing the reaction temperature for pyrolysis of 1 leads to the formation of perfluoro-1,3-cyclohexadiene (7), an irreversible process which occurs readily at 220 °C.



Though they did not discover the thermal electrocyclization to 6, Dědek's group has reported the cyclization to 7 in the temperature range 400–500 °C.[8,20]

In the pyrolysis of 1 the vinylcyclobutene is thus the product of kinetic control, while the cyclohexadiene is the product of thermodynamic control (Figure 2). Why is the free energy of activation for cyclization of 1 to a 4-membered ring lower than that for 6-membered ring formation? Because of the difference in ring strain, the cyclohexadiene must be more stable by many kcal/mol than the cyclobutene. The reason for the striking periselectivity may lie in a combination of steric and electronic effects. Nonbonded repulsion between the inside fluorines at C.1 and C.6 in the disrotatory six-electron transition state, where they are directly opposed, appears to be more severe than corresponding interactions in the conrotatory four-electron process. In addition, Rondan and Houk have predicted that π donor substituents such as fluorine should

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(9) This is also true for hexafluorobutadiene. Brundle, C. R.; Robin, M. B. *J. Am. Chem. Soc.* **1970**, *92*, 5550.

(10) Gavin, R. M., Jr.; Risemberg, S.; Rice, S. A. *J. Chem. Phys.* **1973**, *58*, 3160. These spectra were measured in the vapor phase.

(11) This is typical; see, for example, Philis, J.; Bolovinos, A.; Andritsopoulos, G.; Pantos, E.; Tsekeris, P. *J. Phys. B: At. Mol. Phys.* **1981**, *14*, 3621. Also see ref 9.

(12) Chang, C. H.; Andreassen, A. L.; Bauer, S. H. *J. Org. Chem.* **1971**, *36*, 920.

(13) Hirao, K.; Nakatsuji; H. Kato *J. Am. Chem. Soc.* **1973**, *95*, 31.

(14) Dixon, David A. *J. Phys. Chem.* **1986**, *90*, 2038.

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(16) Dolbier, W. R., Jr.; Koroniak, H.; Burton, D. J.; Bailey, A. R.; Shaw, G. S.; Hansen, S. W. *J. Am. Chem. Soc.* **1984**, *106*, 1871.

(17) Dolbier, W. R., Jr.; Gray, T. A.; Keaffaber, J. J.; Celewicz, L.; Koroniak, H.; *J. Am. Chem. Soc.* **1990**, *112*, 363.

(18) Kirmse, W.; Rondan, N. G.; Houk, K. N. *J. Am. Chem. Soc.* **1984**, *106*, 7989.

(19) Rondan, N. G.; Houk, K. N. *J. Am. Chem. Soc.* **1985**, *107*, 2099.

(20) Chvátal, Z.; Brothankova, M.; Hrabal, R.; Dědek, V. *Czech. CS* **1988**, *241*, 840.

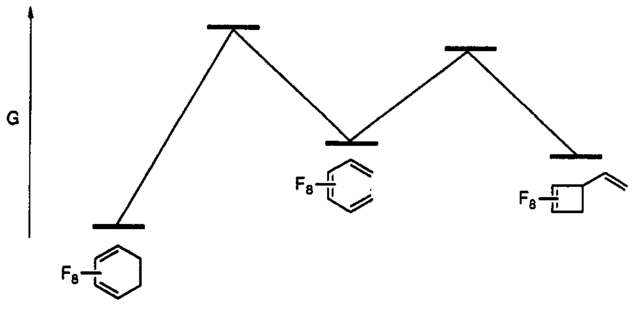
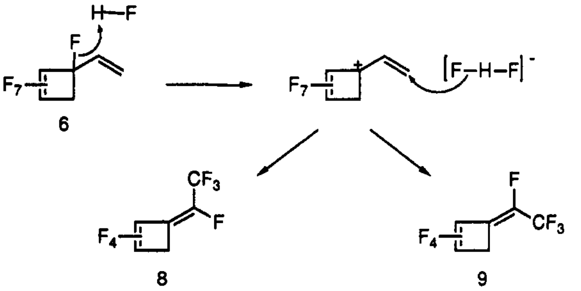


Figure 2. Schematic representation of the energetics for the thermal four- and six-electron cyclizations of *cis*-perfluoro-1,3,5-hexatriene.

Scheme 2

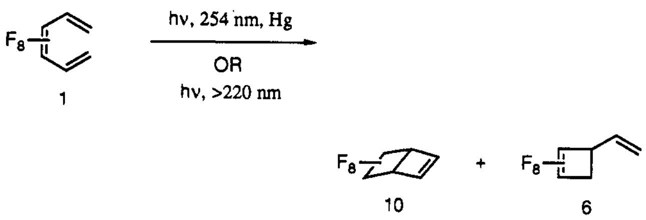


prefer outward rotation in six-electron cyclizations for the same reasons they do in four-electron electrocyclic processes.[19] Since cyclohexadiene formation requires two inward-rotating fluorines but cyclobutene formation only one, the energetic advantage enjoyed by the latter transformation may arise in part from this difference.

The first time an attempt was made to obtain vinylcyclobutene on a preparative scale by pyrolysis of 1 at 160 °C, two new products were obtained instead in a ~1:1 ratio. Analysis of their ^{19}F NMR spectra revealed them to be the stereoisomeric 3-ethylidenecyclobutenes 8 and 9. Their configurations were assigned on the basis of the spin coupling between the CF$_3$ group and the proximal ring fluorine(s). ^{19}F NMR spectrum of 8 (CDCl$_3$): −71.3 (t, $^3J \approx {}^5J$ = 14 Hz, CF$_3$), −112.4 (m, C[2]F), −113.4 (m, CF$_2$), −121.6 (m, C[1]F), −139.6 ppm (m, exocyclic CF). ^{19}F NMR spectrum of 9 (CDCl$_3$): −71.7 (dt, ^3J = 12.5, ^5J = 5.8 Hz, CF$_3$), −111.8 (m, CF$_2$), −116.3 (m, C[2]F), −120.4 (m, C[1]F), −147.9 ppm (m, exocyclic CF).

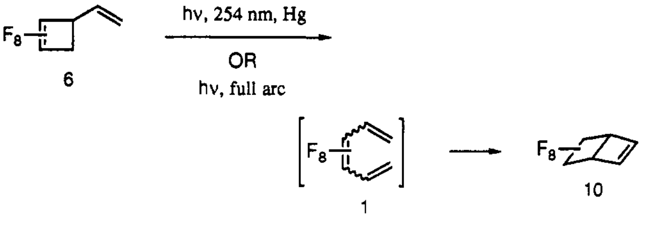
We suspected that a small amount of adventitious hydrogen fluoride was responsible for isomerizing the expected cyclobutene 6, with its tertiary and doubly allylic fluorine, to these stabler isomers (Scheme 2). Consistent with this interpretation, we found that adding some calcium carbonate as an acid scavenger to triene 1 prior to pyrolysis solved the problem, and vinylcyclobutene 6 was obtained cleanly.

Photochemistry. Photolysis of the parent *cis*- and *trans*-1,3,5-hexatrienes in the vapor phase yields a complex mixture, including hydrogen-shift, dehydrogenation, and fragmentation products in addition to the electrocyclization product 1,3-cyclohexadiene.[3] In contrast, *cis*-perfluoro-1,3,5-hexatriene cyclizes cleanly in the vapor phase, yielding a mixture of vinylcyclobutene 6 and perfluorobicyclo[2.2.0]hex-2-ene (10), as reported first by the Prague group. The latter compound arises via photocyclization of initially formed 1,3-cyclohexadiene 7,[21] which we have detected during the course of the reaction. The photoreaction was performed at low pressure with a Vycor-filtered medium-pressure mercury arc, and the ratio of 6 to 10 was 1:1.1.



Surprisingly, the 6 to 10 ratio was also 1:1.1(5) when the photolysis was carried out at low pressure with mercury sensitization using 2537-Å light.[22] Essentially the same ratio was obtained when a bath gas (nitrogen, 550 Torr) was present in addition to the mercury. Thus, even though the vinylcyclobutene was born vibrationally hot, it was not ring-opening or ring-expanding in these experiments. While the direct photolysis is probably a singlet-state reaction, one would expect the mercury-sensitized process to take place via T$_1$ since the excitation is provided by triplet mercury atoms. Though possible, it seems quite unlikely that the same products would form in the same ratio from the S$_1$ and T$_1$ states of the two trienes. (The trienes readily interconvert upon irradiation.) Mercury's ^{3}P$_1$ state lies 112.5 kcal/mol above ground, so sufficient energy is available to excite the trienes to their S$_1$ states. Moreover, spin-forbidden transitions are facile in mercury atoms because spin-orbit coupling here is very large. Together, these considerations suggest the possibility that in this special case mercury sensitization yields singlet excited molecules at least some of the time. Triplet trienes 1 and 2 may not undergo valence isomerization and, hence, may not influence the product composition.[23]

Vinylcyclobutene 6 was subjected in the vapor phase to mercury photosensitization with 254-nm light in the hope of effecting internal [2 + 2] cycloaddition to give highly strained tricyclic fluorocarbons. The sole volatile product of this very slow photoreaction, however, was bicyclohexene 10, formed presumably via ring opening to 1 (and/or 2). The same result was obtained, though more slowly yet, by direct photolysis using an unfiltered medium-pressure mercury arc. Incidentally, mercury sensitization of 10 gave nothing but polymers, so there is no indication that the 6 → 10 transformation is reversible.



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[21] Feast, W. J.; Musgrave, W. K. R.; Weston, R. G. *J. Chem. Soc., Chem. Commun.* **1970**, 1337; **1971**, 709.

[22] The Czech researchers also irradiated 1 in the vapor phase both without and with mercury (ref 8). They noted a large decrease in the 6 to 10 ratio when mercury was present. This result is puzzling, as their irradiation source was a high-pressure mercury arc which would have a reversed line at 2537 Å.

[23] Dědek *et al.* found that irradiation of a roughly 1 M solution of 1 in acetone with a high-pressure mercury arc resulted in partial isomerization to 2, but no valence isomer formation. Both direct and sensitized excitation must have occurred here, since the trienes absorb much more intensely than acetone at the latter's maximum. Therefore, both singlet and triplet excited trienes were generated; apparently neither kind of state yielded valence isomers readily under these conditions.

It is now appropriate to explain our basis for the assignment of configuration to trienes 1 and 2 given at the beginning of this discussion. In principle, this assignment could be made by examining the splitting of the ^{13}C satellites of the ^{19}F NMR signals for the two central fluorines. The satellites should reveal the coupling constant connecting those fluorines, which should be far greater in magnitude if they are trans than if cis. In hexafluorobutadiene, for example, $J_{cis} = 32$ Hz and $J_{trans} = -119$ Hz.[24] Unfortunately, we were not able to observe the satellites clearly. The configurational assignment for the trienes was therefore made on the basis of photochemistry.

Vinylcyclobutene 6 can be generated directly, in principle, from either 1 or 2, but 1,3-cyclohexadiene 7 can form directly only from the cis isomer 1; i.e., 2 must be photoisomerized to 1 before photocyclization to 7 can occur. Whichever triene were chosen as the starting material, if both products arose solely from the cis isomer, the ratio of 7 (plus its cyclization product 10) to 6 would be essentially invariant with irradiation time (until the reaction was almost complete, when it would increase very slowly as 6 was photoisomerized to 10). If 6 were formed at least in part from 2, however, one should observe a *decrease* in the 7-to-6 ratio as the reaction progressed if one started with 1 but an *increase* if one started with 2.

The major isomer obtained from the triene synthesis was irradiated in the vapor phase with very low intensity 254-nm light in order to observe the earliest stages of reaction. After 1 min, about 2% conversion had occurred; the product was 7 plus the other triene isomer. No 6 was detected. After 2 min, 7 and the other triene were each present in ~2% yield, but again no 6 was detectable. When the reaction was carried to completion (360 min), 7 and 10 together comprised 50% of the product and 6 the other 50%. These results show unequivocally that the starting material had the cis configuration. Our findings confirm the conclusions of the Czech authors, who assigned configurations to the two trienes on the basis of ^{19}NMR chemical shift arguments.

Conclusion

Perfluoro-1,3,5-hexatriene isomer 2 was prepared by catalytic isomerization of its stereoisomer 1, and their configurations were assigned as trans and cis, respectively, by a photochemical method. At 13 °C the cis isomer is slightly lower in free energy than the trans. The trans triene is quite stable thermally, but the cis cyclizes periselectively at 160 °C to 3-vinylcyclobutene (6). This reversible reaction has an equilibrium constant of 12 at 160 °C. Electrocyclic opening of 6 is completely stereoselective, yielding only 1. At temperatures over 200 °C, irreversible isomerization of the 1/6 mixture to perfluoro-1,3-cyclohexadiene (7) occurs. Ultraviolet irradiation readily interconverts 1 and 2; both direct and mercury-sensitized vapor-phase photolysis of 1 give 6 and perfluorobicyclo[2.2.0]hex-2-ene (8), which is the photocyclization product of initially formed 7. Mercury sensitization of vinylcyclobutene 6 yields 8 irreversibly. The chemistry of the perfluoro-1,3,5-hexatrienes stands in sharp contrast to that of the parent hydrocarbons.

The configurational assignments, the *high*-temperature cyclization of 1, and the principal results from photolysis of the hexatrienes confirm recently reported findings of the Prague group.

Experimental Section

General Procedure. For thermal and photochemical isomerization studies, pure (>95% purity) *cis*-perfluoro-1,3,5-hexatriene, *trans*-perfluoro-1,3,5-hexatriene, perfluorobicyclo[2.2.0]hexene, and perfluoro-3-vinylcyclobutene were used. To purify these starting materials, preparative GC separations were performed on a Hewlett-Packard 5750 gas chromatograph with a thermal conductivity detector using a 25 × 1/4 column containing 10% SF-96 on 80/100 mesh Chromosorb W-HP-DMCS. Helium was used as a carrier gas. ^{19}F NMR spectra were obtained in $CDCl_3$ either at 282.2 MHz with a Varian XL-300 or at 56.2 MHz with a JEOL FX-60Q Fourier transform spectrometer. Chemical shifs are reported in ppm from internal $CFCl_3$ (Φ scale). Infrared spectra were measured on a Perkin-Elmer 1600 FTIR spectrophotometer. Mass spectra were determined using a Hewlett-Packard 5890 gas chromatograph equipped with HP 5971 mass selective detector. Ultraviolet-visible spectra were recorded on a Perkin-Elmer Lambda 2 spectrophotometer. Vapor-phase photolyses were carried out in quartz round-bottom flasks at 2537 Å in a cylindrical cavity photoreactor equipped with 10 25-W GE-type G25T8 lamps and a cooling fan or with a 450-W Canrad-Hanovia medium-pressure mercury lamp contained in a quartz water jacket.

Reagents and Solvents. Solvents and reagents used in this work were reagent grade, and the solvents were dried following standard procedures. Zinc was activated according to the procedure of Shriner and Newman.[25] Ethanol was purified over sodium and then distilled. 1,2-Dibromo-1-chlorotrifluoroethane was synthesized by the reaction of bromine with chlorotrifluoroethene (PCR).[26] *cis*-Perfluoro-1,3,5-hexatriene was prepared from the photoreaction of 1,2-dibromo-1-chlorotrifluoroethane with chlorotrifluoroethene.[7] The triene was purified by preparative GC.

Perfluoro-3-vinylcyclobutene. A heavy-walled Pyrex ampule containing 1.00 g (4.64 mmol) of *cis*-perfluoro-1,3,5-hexatriene and 0.40 g of $CaCO_3$ was connected to the vacuum line and subjected to two freeze–pump–thaw cycles. The glass bomb was then sealed under vacuum (0.015 Torr) using a torch. The ampule was placed inside a metal pipe wrapped with heating tape and heated to about 160 °C. The temperature was controlled by an Omega temperature controller, Model 149, and monitored by means of a thermocouple attached to the ampule. Pyrolysis was carried out for 20 h; the tube was cracked open after cooling with liquid nitrogen. The contents were then vacuum transferred. Pure perfluoro-3-vinylcyclobutene was isolated in 86% yield (0.86 g) by preparative GC. ^{19}F NMR: −92.4 (dd, $J_1 = 60.5$ Hz, $J_2 = 36.7$ Hz, C[2′]F cis to C[1′]F), −110.6 (ddt, $J_1 = 118.4$ Hz, $J_2 = 60.5$ Hz, $J_3 = J_4 = 16.6$ Hz, C[2′]F trans to C[1′]F), subsplit apparent AB quartet at −114.5 and −116.9 ($J_{app} = 187.5$ Hz, 2F, CF_2), −123.4 (m, C[1]F), −125.3 (d, $J = 7.3$ Hz, C[2]F), −161.7 (m, C[3]F), −185.9 (ddd, $J_1 = 118.4$ Hz, $J_2 = 36.7$ Hz, $J_3 = 23.4$ Hz, C[1′]F). IR: 1788 (s), 1775 (s), 1394 (s), 1341 (m), 1304 (s), 1219 (w), 1164 (s), 1150 (s), 1085 (m), 1009 (s), 944 (w), 869 (w), 834 (w) cm^{-1}. MS *m/e*: 224 (M^+), 205 ($C_6F_7^+$), 186 ($C_6F_6^+$), 174 ($C_5F_6^+$), 155 ($C_5F_5^+$, base), 143 ($C_4F_5^+$), 124 ($C_4F_4^+$), 105 ($C_4F_3^+$), 93 ($C_3F_3^+$), 74 ($C_3F_2^+$), 69 (CF_3^+).

***trans*-Perfluoro-1,3,5-hexatriene.** A glass tube containing 0.500 g (2.23 mmol) of *cis*-perfluoro-1,3,5-hexatriene and a catalytic amount of iodine was positioned inside a cold water jacket. The triene was irradiated by a tungsten lamp for 5 h. Then the cis and trans triene mixture was collected by a vacuum transfer. Pure *trans*-perfluoro-1,3,5-hexatriene was isolated in 36% yield (0.18 g) by preparative GC. ^{19}F NMR: −91.2 (m, 2F, F_a), −104.4 (dm, $J = 115$ Hz, 2F, F_b), −150.8 (narrow m, 2F, F_c), −185.0 (dm, $J = 115$ Hz, 2F, F_d). IR: 1758 (vs), 1530 (w), 1345 (s), 1316 (vs), 1252 (w), 1189 (vs), 1121 (vs), 1028 (s), 1009, 828, 809 cm^{-1}. MS *m/e*: 224 (M^+), 205 ($C_6F_7^+$), 193 ($C_5F_7^+$), 186 ($C_6F_6^+$),

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174 ($C_5F_6^+$), 155 ($C_5F_5^+$), 143 ($C_4F_5^+$), 131 ($C_3F_5^+$, base), 124 ($C_4F_4^+$), 105 ($C_4F_3^+$).

Equilibration of the Trienes. *cis*-Perfluoro-1,3,5-hexatriene (12 mg, 0.054 mmol) and a catalytic amount of iodine were dissolved in $CDCl_3$; the solution was transferred into a NMR tube. The tube was sealed, positioned in a cold water cooling jacket, and irradiated by a tungsten lamp at 13 °C. Trans triene began to form, and the reaction was continued until no further changes occurred in the ^{19}F NMR spectrum. Equilibrium was reached after about 2 h, and the ratio of cis to trans triene was measured by multiple ^{19}F NMR integrations ($K = 0.83$).

Equilibration of the Cis Triene and Perfluoro-3-vinylcyclobutene. Into each of six dried quartz ampules which had been evacuated to 15 mTorr and cooled with liquid nitrogen was transferred 35 mg of >95% pure *cis*-perfluoro-1,3,5-hexatriene. The ampules were degassed by freeze–pump–thaw cycles and sealed by a torch under vacuum. They were immersed in a well-stirred, thermostated oil bath and heated to 160 °C. After a certain time, they were removed from the oil bath and quickly cooled with ice–water. Each ampule was cracked open after cooling with liquid nitrogen, and the contents were dissolved in $CDCl_3$. ^{19}F NMR revealed the presence of cis triene and vinylcyclobutene. The ratio, obtained by multiple ^{19}F NMR integrations of cis triene to vinylcyclobutene decreased with time, but after 20 h remained unchanged at 1:12.2. This value was confirmed by performing a series of pyrolytic experiments on 100% pure vinylcyclobutene under the same conditions.

Pyrolysis of *cis*-Perfluoro-1,3,5-hexatriene. As described above, the cis triene (50 mg, 0.22 mmol) was transferred into a well-dried ampule. The ampule was degassed, sealed under vacuum using a torch, and placed inside a heating pipe. Pyrolysis was performed at 220 °C for 7 h. The clear, colorless contents were dissolved in $CDCl_3$ and analyzed by ^{19}F NMR. Starting triene was gone; vinylcyclobutene and perfluoro-1,3-cyclohexadiene were present in the ratio 1:1.5.

Mercury-Sensitized Vapor-Phase Photolysis of *cis*-Perfluoro-1,3,5-hexatriene. Degassed *cis*-perfluoro-1,3,5-hexatriene (42 mg, 0.19 mmol) was transferred into an evacuated 150-mL quartz round-bottom flask fitted with a stopcock and containing a drop of Hg. The sample rapidly vaporized when warmed to room temperature. The flask was centered in the cavity photoreactor and irradiated for 6 h. On a vacuum line the reaction mixture was dynamically transferred into a U-trap (40 mg, 95%). No high boiling point material (polymeric residue) was found in the flask. ^{19}F NMR spectrum indicated the presence of vinylcyclobutene and its bicyclo[2.2.0] isomer in a 1:1.1(5) ratio. This photoreaction was also performed in the presence of nitrogen as a bath gas. Nitrogen (550 Torr) was introduced into the reaction flask after addition of triene and a drop of Hg. The subsequent procedure was the same as above. ^{19}F NMR showed the ratio of vinylcyclobutene to its bicyclo[2.2.0] isomer was 1:1.(2).

Direct Vapor-Phase Photolysis of *cis*-Perfluoro-1,3,5-hexatriene. As described above, the cis triene (100 mg, 0.446 mmol) was transferred into an evacuated 150-mL quartz round-bottom flask, where it vaporized quickly at room temperature. The flask was positioned as close as possible to the quartz cooling jacket surrounding a Vycor-filtered 450-W medium-pressure Canrad-Hanovia mercury lamp, and the triene was photolyzed for 12 h. When the reaction mixture was transferred into a U-trap, no high boiling material was observed on the bottom of the flask. The ^{19}F NMR spectrum of the colorless distillate showed the presence of both vinylcyclobutene and its bicyclo[2.2.0] isomer in the ratio 1:1.1. Photolysis was also carried out in the presence of a bath gas, and in this experiment the lamp was *unfiltered.* Nitrogen (500 Torr) was introduced into the reaction flask after addition of triene; the subsequent procedure was the same as above. Irradiation was carried out for 4 h. The reaction mixture was subsequently transferred into a U-trap, and no high boiling material was found at the bottom of the flask. The ^{19}F NMR spectrum revealed the presence of both vinylcyclobutene and its isomer in a ratio of 1:1.3.

Table 1. Low-Intensity Photolysis of *cis*-Perfluoro-1,3,5-hexatriene

time (min)	**1** (%)	**2** (%)	**7** (%)	**6** (%)	**10** (%)
1	98.5	0.5	1.0	0	0
2	96.2	2.0	1.8	0	0
360	0.0	0.0	19.0	49.0	32.0

Mercury-Sensitized Vapor-Phase Photolysis of Perfluoro-3-Vinylcyclobutene. Degassed 95% pure perfluoro-3-vinylcyclobutene (40 mg, 0.18 mmol) was transferred into an evacuated 150-mL quartz round-bottom flask fitted with a stopcock and containing a drop of Hg. The flask was centered in the cavity photoreactor, and the fully vaporized sample was photolyzed for 40 h. When the reaction mixture was transferred into a U-trap under vacuum (34 mg, 85%), high-boiling material was found on the bottom of the flask (6 mg, 15%). The ^{19}F NMR spectrum of the contents of the trap indicated the presence of bicyclo[2.2.0] isomer (45%) and the starting material (40%). Perfluoro-3-vinylcyclobutene was also subjected to direct vapor-phase photolysis with the 450-W medium-pressure Canrad-Hanovia mercury lamp using no filter. The subsequent procedure was the same as above; irradiation was carried out for 40 h. When the reaction mixture was transferred into a U-trap, high-boiling material was observed at the bottom of the flask (30%). The trap contents were analyzed by ^{19}F NMR, which showed the presence of the bicyclo[2.2.0] isomer (18%) and starting material (52%).

Mercury-Sensitized Vapor-Phase Photolysis of Perfluoro-[2.2.0]bicyclohexene. As described above, bicyclo[2.2.0] hexene (42 mg, 0.19 mmol) was transferred into an evacuated 150-mL quartz round-bottom flask containing a drop of Hg. The sample rapidly vaporized when warmed to room temperature. The flask was centered in the cavity photoreactor and irradiated for 40 h. On a vacuum line the reaction mixture was dynamically transferred into a U-trap. High-boiling material was found at the bottom of the flask (17 mg, 40%). The ^{19}F NMR spectrum of the transferred liquid revealed only starting material (25 mg, 60% recovery). Vinylcyclobutene was not formed.

Determination of the Configuration of the Perfluoro-1,3,5-hexatrienes. Degassed perfluoro-1,3,5-hexatriene (40 mg, 0.18 mmol), the isomer which was obtained from the literature procedure,[7] was transferred into an evacuated 150-mL quartz round-bottom flask fitted with a stopcock (no Hg). The flask was positioned in the cavity photoreactor equipped with only one 25-W GE-type G25T8 lamp, and the fully vaporized triene was photolyzed. After photolysis, the reaction mixture was dynamically transferred into a U-trap under vacuum. No high boiling point material was observed at the bottom of the flask. Product distribution, product yield, and irradiation times are listed in Table 1. These results reveal that the starting triene had the cis configuration.

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