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Thermal and Photochemistry of Perfluoro-1,6-heptadiene and the Perfluoro-1,3,6-heptatrienes

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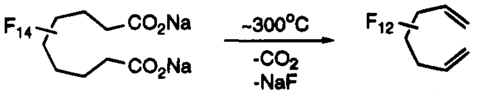
Pyrolysis transformed the title diene (**1**) into a 9:1 mixture of perfluorobicyclo[3.1.1]heptane (**2**) and *cis*-perfluorobicyclo[3.2.0]heptane (**3**) at 300 °C and at >450 °C principally into perfluorocyclopentene (**11**). Mercury-sensitized vapor phase photolysis of **1** also yielded **2** and **3**, but the latter now dominated and its trans isomer **13** was formed as well. In the presence of nitrogen as a bath gas, the product was further enriched in the [3.2.0] isomers. Radical bromination of **1**, a model reaction for the triplet photocyclization, gave *cis*- and *trans*-perfluoro-1,2-bis(bromomethyl)-cyclopentane (**16**). Configurations were assigned to the cis and trans isomers of perfluoro-1,3,6-heptatriene (**19** and **20**), and they were equilibrated with iodine/visible light ($K_{t\to c} = 1.6(7)$ in CDCl$_3$, 14 °C). The cis triene underwent electrocyclization at 133 °C to perfluoro-3-allylcyclobutene (**27**); thermal ring opening of this cyclobutene yielded exclusively the cis isomer. At 250 °C both the cis triene and the allylcyclobutene were transformed quantitatively into perfluorobicyclo[3.1.1]hept-2-ene (**28**) . Trans triene gave no detectable cyclobutene over a range of temperatures, but yielded the [3.1.1] compound at 250 °C. Ultraviolet irradiation of cis triene produced the allylcyclobutene, and mercury photosensitization of either compound (or the trans triene) proceeded a step farther to give tricycloheptane valence isomers (**31** and **32**). The internal [2 + 2] cycloadditions described here contribute to our knowledge of the ground rules for reactions of this type in unsaturated fluorocarbons.

By investigating the thermal and photochemical behavior of some simple perfluoro dienes and polyenes, we wish to establish ground rules for their reactivity which will have predictive value for this whole class of fluorocarbons. Their chemistry contrasts with that of their hydrocarbon counterparts in interesting ways. For thermodynamic reasons the fluorocarbons have a much greater tendency to undergo internal cycloaddition reactions, and their thermal and photochemistry is often cleaner owing to a lesser tendency to polymerize and to undergo atom abstraction and migration reactions.[2−6] The present paper extends our earlier work on unsaturated 6-carbon fluorocarbons[2−4] to 7-carbon homologs.

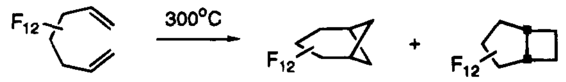
Results and Discussion

Perfluorohepta-1,6-diene (1). This diene[7] was synthesized in good yield by pyrolysis of the sodium salt (**2**) of perfluoroazelaic acid,[8] which has recently become commercially available:

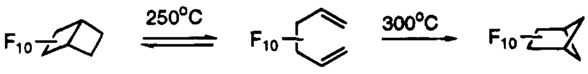


1

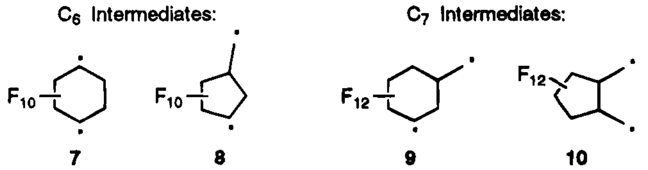
Pyrolysis of **1** in Pyrex ampules at 300 °C required about 1 day for completion. The diene was transformed into a clear, colorless liquid composed of perfluorobicyclo[3.1.1]heptane (**2**) and perfluorobicyclo[3.2.0]heptane (**3**) in the ratio 9:1. These isomers are easily distinguished by ^{19}F NMR, as the spectrum of **2** features a single AB-like quartet while that of **3** shows three such quartets (C_{2v} and C_s symmetry, respectively). Compare the pyrolytic behavior of **1** with that of perfluoro-1,5-hexadiene (**4**), which forms the bicyclo[2.2.0] isomer **5** reversibly at 250 °C and at higher temperatures yields the [2.1.1] isomer **6**.[2] Parallel cycloaddition of the double bonds is much faster than crosswise cycloaddition in the 6-carbon case, but the opposite is true in the 7-carbon case. This apparent contrast is not surprising but, in fact, reflects a mechanistic similarity. These reactions are stepwise processes which proceed via biradical intermediates; in both cases the favored pathways proceed via 6-membered ring biradicals (**7** and **9**) and the higher energy paths via 5-membered rings (**8** and **10**). As noted earlier,[2] this can be understood as a reflection of the smaller strain energy



1 **2** 9 : 1 **3**



5 **4** **6**



7 **8** **9** **10**

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[1] Present address: 3M Industrial and Consumer Sector Research Laboratory, 3M Center Bldg. 201-1W-28, St. Paul, MN 55144-1000.

[2] Correa, R. A.; Jing, N.; Lemal, D. M. *J. Org. Chem.* **1993,** *58,* 6406.

[3] Jing, N.; Lemal, D. M. *J. Org. Chem.* **1994,** *59,* 1844 .

[4] Jing, N.; Lemal, D. M. *J. Am. Chem. Soc.* **1993,** *115,* 8481.

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

[6] Dolbier, W. R., Jr.; Palmer, K. W. *Tetrahedron Lett.* **1993,** 6201.

[7] Fearn, J. E. *J. Res. Nat. Bur. Stand. Sect. A* **1971,** *75,* 41.

[8] This method is discussed in: Hudlicky, M. *Chemistry of Organic Fluorine Compounds,* 2nd ed.; Ellis Horwood: Chichester, England, 1976; pp 498−500.

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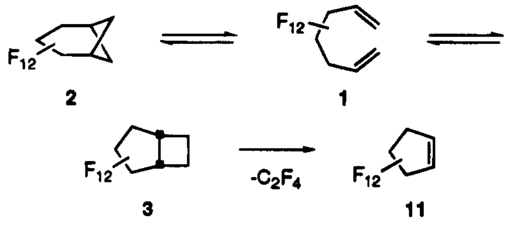
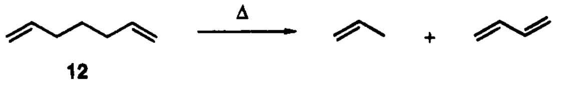
in 6-rings and correspondingly lower transition state energies for biradical formation.

When diene **1** is pyrolyzed at temperatures above 300 °C, the ratio of **2** to **3** diminishes. By 400 °C it has dropped to 4:1, and a small amount of perfluorocyclopentene (**11**) has appeared in the product. At 450 °C, the composition of the mixture after 20 h is roughly 1:1:2 (**2**:**3**:**11**). Flash vacuum pyrolysis of **1** in a quartz tube at 750 °C gives cyclopentene **11** in >90% yield, and tetrafluoroethylene is detected as a byproduct. Apparently the [3.1.1] compound **2** interconverts with the [3.2.0] heptane **3** via diene **1** at very high temperatures, and **3** fragments into cyclopentene **11** and tetrafluoroethylene. Consistent with this interpretation is the finding that both **2** and **3** yield **11** when heated at 450 °C.



The parent 1,6-heptadiene (**12**) displays very different pyrolytic behavior from that of diene **1**, for it fragments at 400–450 °C via a *retro*-ene reaction to give propylene and butadiene.[9] There is a very minor side reaction which resembles the fluorocarbon's thermal chemistry, however: reversible formation of bicyclo[3.2.0]heptane, which fragments into cyclopentene and ethylene.

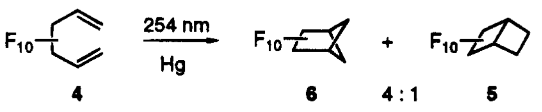


Direct photolysis of diene **1** with an unfiltered medium pressure mercury arc results in polymerization. In contrast, mercury-sensitized photolysis of the diene yields **2** and **3**, as in thermolysis. But now the minor thermolysis product **3** is dominant, and a substantial amount of its trans isomer (**13**) is also formed (**2**:**3**:**13** = 2.8:5.7:1.0).

13

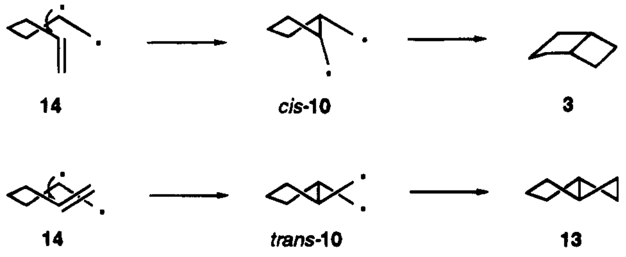
Since **13** has C_2 symmetry, it is distinguishable from the cis isomer (**3**) by the fact that the fluorines at C_3 give rise to a singlet in the ^{19}F NMR spectrum, whereas those in **3** appear as an AB quartet.

The fact that 5-membered-ring dominates over 6-ring biradical formation in the photolysis of **1** (i.e., **10** vs **9**) contrasts with the thermal chemistry, but agrees nicely with the photolysis results we obtained with perfluoro-1,5-hexadiene (**4**): here, too, 5-ring took precedence over



6-ring biradical generation (**8** vs **7**).[2] This agreement supports the conclusion that while the thermal chemistry of these dienes is controlled by relative biradical stability, the photochemistry is dominated by kinetic considerations. This dichotomy can be understood with the help of the Hammond postulate. Since biradical formation from the ground state of the diene is strongly endothermic, the transition states come late and therefore reflect relative biradical energies. On the other hand, biradical generation from the triplet state is very exothermic, and the consequently early transition states are influenced by factors other than biradical stability. If the triplet state of the diene can be adequately represented as the biradical **14**, the favored mode of internal attack should

Scheme 1



All structures perfluorinated.

be predictable from the behavior of monoradicals. Attack by the radical center C_2 is favored entropically over that by C_1, and for stereoelectronic reasons C_2 should prefer attack at C_6 over C_7 (see arrows). Ample precedent for the latter surmise is provided by the many examples of 5-hexenyl radicals cyclizing to cyclopentylmethyl radicals.[10] Preferential formation of 5-membered ring biradicals exemplifies Srinivasan's "rule of five", which correctly predicts the course of a great many photoreactions.[11]

trans-Perfluorobicyclo[3.2.0]heptane (**13**) is highly strained; in fact, ab initio calculations at the 6-31G* level (based on AM-1-optimized geometries)[12] indicate that **13** lies 21.9 kcal/mol above cis isomer **3** and 22.0 kcal/mol above **2**. Formation of **13** is not surprising, though, as models indicate that the cis and trans isomers of **10** should form with comparable ease (Scheme 1). In other words, the differential strain does not get introduced until the very exothermic second step in which the biradical collapses to product.

In the presence of nitrogen (560 Torr) as a bath gas, mercury photosensitization of **1** yields the same three products as in its absence, but now their ratio is **2**:**3**:**13** = 1.0:3.6:1.0. Both the [3.1.1] and cis [3.2.0] isomers diminish relative to the trans [3.2.0], but the first loses disproportionately. This finding can be accommodated by the following ideas. Suppose that, in the absence of bath gas to remove excess energy, much of the biradical *trans*-**10** which is formed upon mercury photosensitization reverts to starting diene because the radical centers are well separated. This would explain why **13** gains with respect to both **2** and **3** in the presence of nitrogen.

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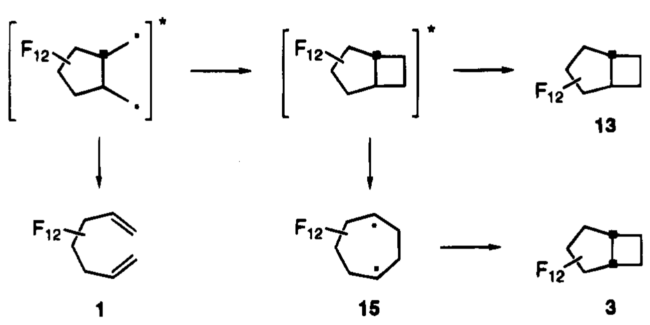
(9) Egger, K. W.; Vitins, P. *J. Am. Chem. Soc.* **1974**, *96*, 2714.

(10) Beckwith, A. L. J.; Ingold, K. U. In *Molecular Rearrangements*; de Mayo, P., Ed.; Academic Press: New York, 1978; Vol. 2.

(11) Schuster, D. I.; Lem, G.; Kaprinidis, N. A. *Chem. Rev.* **1993**, *93*, 3 and references therein.

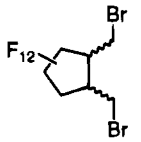
(12) The calculations were performed using the Spartan package of programs (Hehre W. Wavefunction, Inc., 18401 Von Karman, Suite 370, Irvine, CA 92717).

Scheme 2



If one further supposes that the vibrationally hot **13** formed upon closure of *trans*-**10** isomerizes in part to the cis isomer **3** if it is not collisionally deactivated, the increase in **3** relative to **2** in the presence of nitrogen can also be understood (Scheme 2). Support for the latter idea is provided by the observation that **13** isomerizes cleanly to **3** at 300 °C via scission of the very strained central C−C bond to give **15**, which rebonds after inversion of one radical center. [Reversion of **13** to diene **1** cannot be a significant pathway for this thermal isomerization, as that would lead principally to **2**].

We have examined a model reaction for the photosensitized cyclization of **1**; namely, the visible light-promoted addition of bromine to this diene. At high concentrations of bromine both cyclic dibromides (**16**) and acyclic tetrabromides (**17**) are formed in comparable amounts, but in moderately dilute carbon tetrachloride solution tetrabromide formation is effectively suppressed. As expected, the tetrabromides are an approximately equimolar mixture of the *dl* and meso forms, as determined by ^{19}F NMR spectroscopy. The dibromides are a 2:1 mixture of *cis*- and *trans*-**16**, formed via cyclization of the intermediate radical **18**. This unimolecular process outcompetes 1,2-dibromide formation (which leads on to tetrabromide) by attack of **18** on Br$_2$ unless the concentration of the latter is high.[13,14] The cyclization of **18** bears a close similarity to that of **1** in its triplet state, as represented by **14**, and in each case cis product is favored over trans (2:1 for **18** vs 3.6:1 for **14**). The lesser cis-selectivity in the case of bromine addition may reflect the greater bulk at C$_1$ in **18** relative to **14**.



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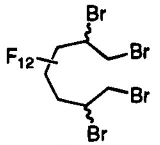

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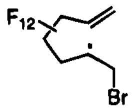
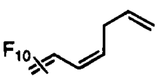


18

***cis*- and *trans*-Perfluoro-1,3,6-heptatriene (19 and 20).** Our interest in these trienes was piqued by the possibility that their photolysis might engage all three double bonds and lead to highly strained tricyclic products. This does not occur with the simplest perfluorotriene, perfluoro-1,3,5-hexatriene (**21**), which gives 3-vinylcyclobutene (**22**) and (via perfluoro-1,3-cyclohexadiene, **23**) perfluorobicyclo[2.2.0]hex-2-ene (**24**).[3,5] The cyclobutene is slowly transformed into **24**, presumably via the original triene. Since trienes **19** and **20** do not have available a pathway analogous to the **21** → **24** transformation, which requires full conjugation of the double bonds, the prospect of their yielding tricyclics seemed hopeful.



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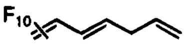

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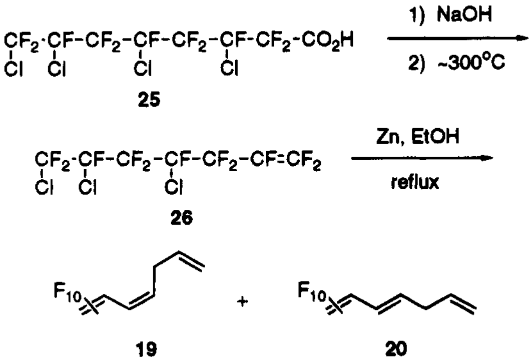
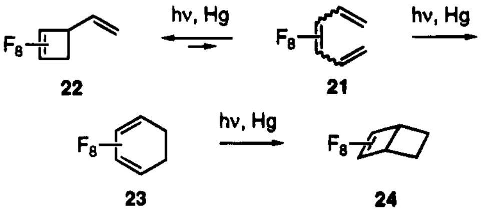
Scheme 3





Trienes **19** and **20** were synthesized from perfluoro-3,5,7,8-tetrachlorooctanoic acid (**25**) via pyrolysis of its sodium salt, which yielded perfluoro-4,6,7-trichloro-1-heptene (**26**).[7] Dechlorination of **26** with zinc in refluxing ethanol gave an equimolar mixture of *cis*-perfluoro-1,3,6-heptatriene (**19**) and its trans isomer (**20**) in 79% yield (Scheme 3).[15] Small amounts of 4-chloro-[7,16] and 4*H*-perfluoro-1,6-heptadiene were also obtained. These two products were avoided when the solvent was diglyme, but the dechlorination was much slower. At 120−130 °C in this solvent, the reaction gave perfluoro-3-allylcyclobutene (**27**, 60%) and perfluorobicyclo[3.1.1]hept-2-ene (**28**, 4%), both cyclization products of the absent cis triene **19** (see below). In addition, the trans triene (**20**) was obtained in 28% yield.

We assigned the configurations of the trienes on the basis of their ^{19}F NMR spectra. The fluorines at C$_3$ and C$_4$ are coupled with $J = {\sim}31$ Hz in the cis isomer, but $J = 140$ Hz in the trans.[17,18] The two heptatrienes were equilibrated at 14 °C in CDCl$_3$ through the agency of iodine and a tungsten lamp, and the cis isomer (**19**) was found to be slightly more stable than the trans (**20**): $K_{c/t}$

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[13] In the radical polymerization of diene **1**, the ratio of cyclized to noncyclized monomer units is >200 (ref 7).

[14] For radical reactions of the parent 1,6-heptadiene which result in cyclopentane formation, see: Brace, N. O. *J. Org. Chem.* **1967**, *32*, 2711, 2879.

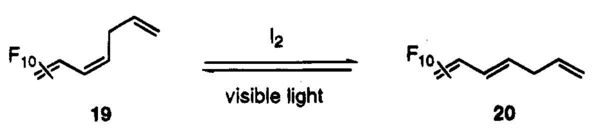
[15] The trienes had been obtained earlier in 27% yield by zinc reduction in diethylene glycol monomethyl ether. Cook, E. W. *Synthesis* **1971**, 369.

[16] Johncock, P. *Synthesis* **1977**, 551. Park, J. D.; Lacher, J. R. *WADC Tech. Rept. 56-590,* **1957**, Part 1, 21.

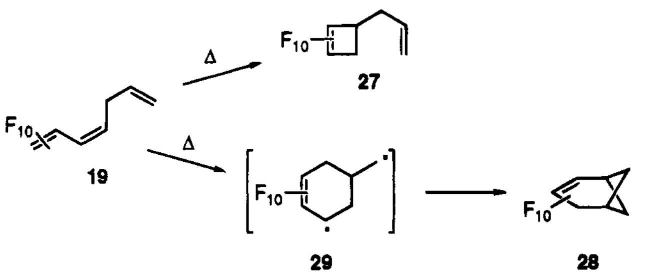
[17] In hexafluorobutadiene, for example, $J_{\text{cis}} = 32$ Hz and $J_{\text{trans}} = (-)119$ Hz. Manatt, S. L.; Bowers, M. T. *J. Am. Chem. Soc.* **1969**, *91*, 4381. Barlow, M. G.; Cheung, K. W. *J. Chem. Soc. B* **1970**, 525.

[18] Configurational assignments had been made for the trienes on the basis that one isomer displayed a single band in the double bond stretching region of the IR spectrum, while the other displayed two (ref 15). The isomer showing the single band was assigned the trans configuration on the grounds that it possessed an "approximate center of symmetry". We found three bands for the trans isomer and two for the cis (see Experimental Section).

= 1.6(7). Equilibration of the perfluoro-1,3,5-hexatrienes produced a similar result.[3] Two analogies provide a context for these counterintuitive findings. First, since even perfluorobutadiene prefers a highly nonplanar conformation,[19] the trans triene isomers presumably do not enjoy the advantage of planarity over the cis as is the case for hydrocarbon di- and polyenes. Second, whatever causes *cis*-1,2-difluoroethylene to be more stable than its trans isomer, a much-debated matter,[20] is probably also at work on the internal double bonds of these trienes.

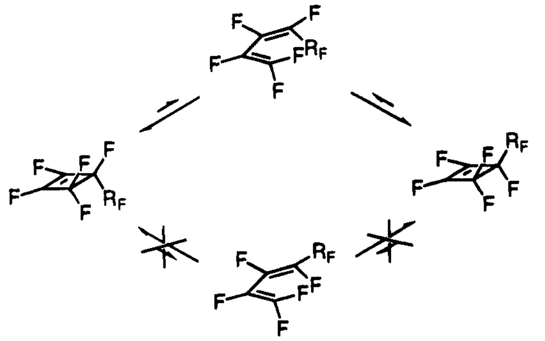


When heated in a sealed ampule at 134 °C for 22 h, cis triene **19** was completely transformed into a 14:1 mixture of cyclobutene **27** and bicycloheptene **28**. At 200 °C for 24 h, triene **19** yielded a 1:1 mixture of these fluorocarbons, and at 250 °C for 22 h, it gave a quantitative yield of **28**. Clearly the cyclobutene, formed reversibly via a 4-electron pericyclic process, is almost the sole product when the reaction is kinetically controlled; but the bicyclic olefin, generated stepwise via biradical **29**, is far more stable.[21] Heating **27** at 250 °C transformed it completely into **28**. Though formation of the [3.1.1] compound is much slower than the electrocyclization, it is dramatically faster than formation of its saturated analog **2** from diene **1**, which proceeds slowly at 300 °C. The contrast is understandable in light of the difference in stability between biradical intermediate **29**, which enjoys allylic stabilization, and the saturated biradical **9**.



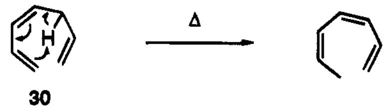
Trans triene **20** also gave **28** in about 50% yield, together with polymer, when heated at 250 °C for 20 h. To produce **28**, triene **20** must have first isomerized to **19**, perhaps via cyclobutene formation (though catalysis by a trace impurity has not been ruled out). Interestingly, however, triene **20** was recovered entirely unchanged when heated for 25 h at 181 °C, a temperature at which **19** cyclizes quickly. Had a significant amount of **20** been formed in the reaction of **19** at 200 °C, it would have been detectable, yet none was found despite the fact that cyclobutene **27** was ring opening readily at that temperature. Both the reluctance of the trans isomer to cyclize and its failure to accumulate as the cyclobutene opened are evidence for very clean torquoselectivity:[22] cyclization occurs at moderate temperatures only if the fluorine substituent at C_4 is "outside" as the new ring begins to form, and opening of the ring occurs exclusively in the direction which rotates the fluorine outward, regenerating the cis isomer (as required for microscopic reversibility) (Scheme 4). Rondan and Houk[23] have explained the well-documented tendency of fluorine and other donor substituents to behave this way in terms of a destabilizing interaction with the transition state HOMO when the substituent is "inside" and a stabilizing interaction with the LUMO when "outside". Ring opening of vinylcyclobutene **22** was also found to be highly torquoselective.[3]

Scheme 4



In the presence of iodine as a catalyst, the unreactive trans triene **20** is transformed quantitatively in 24 h at 130 °C into cyclobutene **27** and bicycloheptene **28** in the ratio 14:1. Iodine thus effects trans → cis isomerization about the internal double bond, leading to the same product mixture found starting from pure cis isomer.

Not surprisingly, the thermal behavior of triene **19** stands in sharp contrast to that of the parent hydrocarbon (**30**), which simply undergoes a [1,5]-sigmatropic shift of hydrogen to bring all three double bonds into conjugation.[24] For the hydrocarbon, cyclization to 3-allylcyclobutene or bicyclo[3.1.1]hept-2-ene would be unfavorable thermodynamically; for the fluorocarbon, the 1,5-shift is not feasible because of the great reluctance of fluorine to engage in atom transfer processes.



Direct photolysis of triene **19** with an unfiltered medium pressure mercury arc gave cyclobutene **27** very cleanly, but mercury-sensitized photolysis proceeded beyond this stage. Whether the starting material was cis triene **19**, trans triene **20**, or cyclobutene **27**, irradiation at 254 nm in the presence of mercury yielded a mixture containing perfluorotricyclo[2.2.1.0^{2,5}]heptane (**31**) (10−15% yield), together with much polymeric material. A small amount of a compound identified solely

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(19) Chang, C. H.; Andreassen, A. L.; Bauer, S. H. *J. Org. Chem.* **1971**, *36*, 920. Hirao, K.; Nakatsuji; H. Kato *J. Am. Chem. Soc.* **1973**, *95*, 31. Dixon, David A. *J. Phys. Chem.* **1986**, *90*, 2038.

(20) Smart, B. E. In *Molcular Structure and Energetics*; Liebman, J. F., Greenberg, A., Eds.; VCH Publishers: Deerfield Beach, FL, 1986; Vol. 3, p 141.

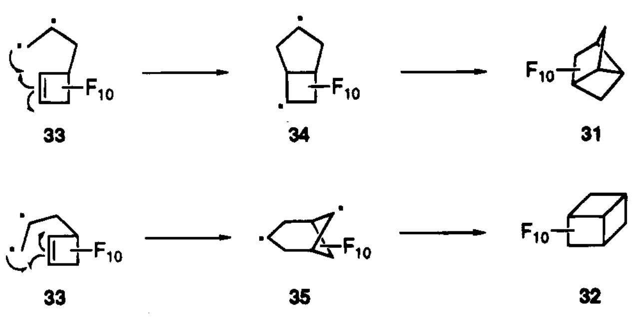
(21) In the case of *cis*-perfluoro-1,3,5-hexatriene, thermal 4-membered-ring formation is much faster than 6, even though both processes are pericyclic and the latter is far more exothermic (ref 3).

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

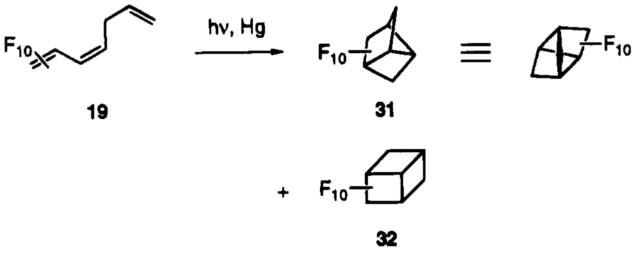
(23) Rondan, N. G.; Houk, K. N. *J. Am. Chem. Soc.* **1985**, *107*, 2099. Kirmse, W.; Rondan, N. G.; Houk, K. N. *J. Am. Chem. Soc.* **1984**, *106*, 7989.

(24) Sellers, S. F.; Dolbier, W. R., Jr.; Koroniak, H; Al-Fekri, D. M. *J. Org. Chem.* **1984**, *49*, 1033.

Scheme 5



by ^{19}F NMR as perfluorotricyclo[3.1.1.0^{3,6}]heptane (**32**) was also obtained. The C_2 symmetry of **31** and the C_{3v} symmetry of **32** aided in their identification. Though yields in this particular system are low, these experiments show that the internal cycloaddition theme can be extended beyond the formation of bicyclics to the creation of highly strained polycyclic structures.



If one represents the triplet state of **27** as **33**, the pathways by which the tricycloheptanes are probably formed can be depicted as shown in Scheme 5. Generation of **31** is initiated by formation of a new 5-membered ring, and the less favored **32** arises via initial formation of a new 6-membered ring. Cyclobutene **27** is a 1,5-diene, and these steps closely parallel the mercury-sensitized photochemistry of perfluoro-1,5-hexadiene (**4**) itself, which gives bicyclohexanes **6** and **5** (4:1 ratio) via 5- and 6-membered ring biradicals, respectively.[2]

Conclusion

Both the thermal and photochemistry of diene **1** are mechanistically congruent with those of its lower homolog **4**. In thermolyses, 6-membered ring biradical formation is favored over 5, whether the result be parallel or crosswise cycloaddition of the double bonds. On the other hand, in triplet state reactions 5-ring biradicals predominate over 6 whether cycloaddition occurs in parallel or crosswise fashion. The photocyclization of diene **27** also obeys this generalization.

Mercury photosensitization of diene **1** yields the very strained trans [3.2.0] bicyclic (**13**) as well as **3** and **2**. At 300 °C **13** isomerizes cleanly to **3**, and at higher temperatures **3** fragments into perfluorocyclopentene (**11**) and tetrafluoroethylene. Bromination of **1** in moderately dilute solution gives 5-membered ring dibromides almost exclusively.

Cis triene **19** is readily interconverted with its trans isomer **20** by iodine, and **19** is the more stable form. Thermolysis of **19** yields allylcyclobutene **27** reversibly at low temperatures and gives exclusively the [3.1.1] bicyclic **28** at higher temperatures. Cyclobutene **27** ring opens thermally with complete torquoselectivity to **19**. Consistent with that finding, trans isomer **20** fails to yield any **27** under conditions where **19** cyclizes rapidly, but gives **28** at sufficiently high temperatures. While direct photolysis of **19** yields **27**, mercury photosensitization of **19**, **20**, or **27** results in further cyclization, producing tricycloheptanes **31** and **32**.

Experimental Section

General Procedure. For thermal and photochemical isomerization studies, pure (>95% purity) perfluoro-1,6-heptadiene, *cis*-perfluoro-1,3,6-heptatriene, *trans*-perfluoro-1,3,6-heptatriene, perfluorobicyclo[3.1.1]heptane, and perfluoro-3-allylcyclobutene 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 ft × 1/4 in. column containing 10% SF-96 on 80/100 mesh Chromosorb W-HP-DMCS. Helium was used as 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 shifts are reported in ppm from internal $CFCl_3$ (Φ scale, upfield negative). Infrared spectra were measured in $CDCl_3$ on a Perkin-Elmer 1600 FTIR spectrophotometer. Low-resolution mass spectra were determined using a Hewlett-Packard 5890 gas chromatograph equipped with HP 5971 mass selective detector. 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. Pyrolyses at temperatures above 200 °C were performed in a metal pipe wrapped with a heating tape. The temperature was controlled by an Omega temperature controller, Model 149, and monitored by means of a thermocouple attached to the ampule. Lower temperature pyrolyses were carried out in a stirred oil bath whose temperature was controlled similarly.

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. Ethylene glycol dimethyl ether was distilled from lithium aluminum hydride. Perfluoroazelaic acid was purchased from Exfluor Research Corp., Austin, TX, and perfluoro-3,5,7,8-tetrachlorooctanoic acid was obtained as a gift from the 3M Company, St. Paul, MN.

Perfluoro-1,6-heptadiene (1). In a 100 mL beaker, perfluoroazelaic acid (5.00 g, 11.4 mmol) was neutralized with 8 N aqueous NaOH. The solution was vigorously stirred and became very viscous. It was evaporated to dryness in a vacuum desiccator at 1 Torr overnight, leaving the sodium salt as a white solid. The salt was pyrolyzed at about 300 °C and 1 Torr in a glass tube connected to a cooled trap immersed in liquid nitrogen. Pyrolysis took place smoothly and was carried out for 6 h. The trap was removed from liquid nitrogen, and CO_2 started bubbling out when the reaction mixture warmed. The crude diene was purified by a vacuum transfer, yield 2.2 g (62%) of 90% pure perfluoro-1,6-heptadiene. It was further purified by preparative GC. ^{19}F NMR: −87.9 (m, 2F, C_1, C_7, cis to F), −105.1 (m, 2F, C_1, C_7, trans to F), −118.7 (s, 4F, C_3, C_5), −126.1 (s, 2F, C_4), −189.0 (m, 2F, C_2, C_6). IR: 1778 (vs), 1360 (vs), 1316 (vs), 1242 (w), 1194 (vs), 1110 (s), 1057 (s), 948 (w), 833 (s), 789 cm^{-1} (w). MS *m/e*: 312 (M^+, $C_7F_{12}^+$), 293 ($C_7F_{11}^+$), 243 ($C_6F_9^+$), 224 ($C_6F_8^+$), 193 ($C_5F_7^+$), 181 ($C_4F_7^+$), 162 ($C_4F_6^+$), 131 ($C_3F_5^+$, base), 93 ($C_3F_3^+$), 69 (CF_3^+).

Pyrolysis of Perfluoro-1,6-heptadiene. ***At 300 °C.*** A heavy-walled Pyrex ampule containing 45 mg (0.14 mmol) of pure perfluoro-1,6-heptadiene was connected to the vacuum line and subjected to two freeze−pump−thaw cycles. The glass bomb was then sealed under vacuum using a torch and heated at 300°C for 36 h. After being cooled with liquid nitrogen the tube was cracked open . The clear, colorless product was dissolved in $CDCl_3$; ^{19}F NMR revealed the

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(25) Shriner, R. L.; Newman, R. W. *Organic Syntheses*; Wiley: New York, 1955; Collect. Vol. III, p 73.

presence of perfluorobicyclo[3.1.1]heptane (**2**) and *cis*-perfluorobicyclo[3.2.0]heptane (**3**) in the ratio 9:1. Starting diene had entirely disappeared. Perfluorobicyclo[3.1.1]heptane. ^{19}F NMR: −118.5 (s, 2F, C_3), −119.7 (s, 4F, C_2, C_4), subsplit apparent AB quartet at -121.0, −135.8 (J_{app} = 234 Hz, 4F, C_6, C_7), −212.7 (s, 2F, C_1, C_5). IR: 1391 (w), 1344 (m), 1327 (s), 1317 (s), 1298 (s), 1275 (s), 1247 (s), 1234 (s), 1213 (s), 1185 (s), 1145 (s), 1002 (m), 982 (m), 966 cm^{-1} (s). MS *m/e*: 293 ($C_7F_{11}^+$), 243 ($C_6F_9^+$), 224 ($C_6F_8^+$), 205 ($C_6F_7^+$), 193 ($C_5F_7^+$), 162 ($C_4F_6^+$), 131 ($C_3F_5^+$, base), 100 ($C_2F_4^+$), 69 (CF_3^+). *cis*-Perfluorobicyclo[3.2.0]heptane: subsplit apparent AB quartet at −120.6, −123.8 (J_{app} = 234 Hz, 4F, C_6, C_7), subsplit apparent AB quartet at -121.3, −130.8 (J = 274 Hz, 4 F, C_2, C_4), subsplit AB quartet at −127.1, −142.5 (J = 265 Hz, 2F, C_3), −204.2 (s, 2F, C_1, C_5). IR: 1340 (s), 1318 (s), 1277 (s), 1235 (m), 1210 (s), 1186 (s), 1036 (m), 1019 (s), 966 (s), 950 (m), 867 (m), 8858 (m), 597 cm $^{-1}$ (m). MS *m/e*: 293 ($C_7F_{11}^+$), 243 ($C_6F_9^+$, base), 224 ($C_6F_8^+$), 212 ($C_5F_8^+$), 193 ($C_5F_7^+$), 162 ($C_4F_6^+$), 131 ($C_3F_5^+$), 124 ($C_4F_4^+$), 100 ($C_2F_4^+$), 93 ($C_3F_3^+$), 69 (CF_3^+). A negative ion mass spectrum measured on a mixture of the two bicycloheptane isomers showed peaks at *m/e* 312 (M^-), 293 (C_7-F_{11}^-), 274 ($C_7F_{10}^-$), 255 ($C_7F_9^-$). HRMS *m/e*: 311.9812 (theor 311.9808).

A 400 mg (1.28 mmol) sample of perfluoro-1,6-heptadiene was pyrolyzed at 300 °C for 36 h as described above. Perfluorobicyclo[3.1.1]heptane was obtained in 90% yield and *cis*-perfluoro[3.2.0]heptane in 10% yield.

At 400 °C. Perfluoro-1,6-heptadiene (40 mg, 0.13 mmol) was pyrolyzed at 400 °C for 23 h. ^{19}F NMR indicated the formation of perfluorobicyclo[3.1.1]heptane and perfluorobicyclo-[3.2.0]heptane in the ratio 4:1, and a small amount of perfluorocyclopentene was also observed.

At 450 °C. The diene (40 mg, 0.13 mmol) was pyrolyzed at 450 °C for 20 h as described above. ^{19}F NMR indicated the formation of perfluorobicyclo[3.1.1]heptane and perfluorobicyclo-[3.2.0]heptane in the ratio 1:1, and now perfluorocyclopentene (**11**) comprised about half of the product. No polymerized product was observed.

Pyrolysis of Perfluorobicyclo[3.2.0]heptane (3 and 13). A mixture of *cis*- and *trans*-perfluorobicyclo[3.2.0]heptane (40 mg, 0.13 mmol) was pyrolyzed at 450 °C for 22 h as described above. ^{19}F NMR demonstrated that the starting bicyclic compounds had disappeared and perfluorocyclopentene had formed in 85% yield.

Pyrolysis of Perfluorobicyclo[3.1.1]heptane (2). A mixture of perfluorobicyclo[3.1.1]- and *cis*-perfluorobicyclo-[3.2.0]heptane in the ratio 9:1 (60 mg, 0.2 mmol) was pyrolyzed at 450 °C for 22 h as above. Starting material had entirely disappeared, as revealed by ^{19}F NMR, and perfluorocyclopentene was present in 78% yield.

Flash Vacuum Pyrolysis of Perfluoro-1,6-heptadiene. Flash vacuum pyrolysis of perfluoro-1,6-heptadiene was carried out using an open quartz tube (65 mm long, 5 mm i.d.) at 1 Torr. A glass sample tube was connected to the inlet of the quartz tube, and the outlet was connected to a liquid nitrogen trap. The diene sample (45 mg, 0.14 mmol) was placed in the glass tube and degassed. Then the sample tube was immersed in an ice bath to control the vapor pressure of the starting diene. The perfluorodiene was allowed to volatilize and pass through the thermolysis tube at 650 °C; the temperature was controlled by an Omega temperature controller, Model 149, and monitored by means of a thermocouple attached to the quartz tube. Trap contents were dissolved in $CDCl_3$ and analyzed by ^{19}F NMR, which showed the formation of *cis*-perfluorobicyclo[3.2.0]heptane (12%), the [3.1.1] compound (23%), perfluorocyclopentene (5%), and recovered starting diene (60%); a trace amount of tetrafluoroethylene was also found. Flash vacuum pyrolysis was also performed at 750 °C as described above. The diene (42 mg, 0.14 mmol) reacted completely, and ^{19}F NMR revealed perfluorocyclopentene (90%) and tetrafluoroethylene as the major products; both perfluorobicyclo[3.2.0] and [3.1.1.]heptane were also formed as minor products (10% yield total) in the ratio 2.5:1.

Flash Vacuum Pyrolysis of Perfluorobicyclo[3.1.1]-heptane. As described above, the bicycloheptane (45 mg, 0.13 mmol) was subjected to FVP at 1 Torr and 740 °C. No residue was visible in the pyrolysis tube, and the product composition by ^{19}F NMR was 32% perfluoro-1,6-heptadiene, 8% perfluorocyclopentene, 10% perfluorobicyclo[3.2.0]heptane, and 49% recovered starting material.

Thermal Isomerization of *trans*- to *cis*-Perfluorobicyclo[3.2.0]heptane. A mixture of *cis*- and *trans*-perfluorobicyclo[3.2.0]heptane in the ratio 8:1 (also including some perfluorobicyclo[3.1.1]heptane) (30 mg, 0.096 mmol) was placed in a heavy-walled Pyrex ampule, degassed, sealed, and heated at 300 °C for 22 h. Analysis of the contents by ^{19}F NMR showed that all of the trans isomer had been converted to the cis isomer.

Mercury-Sensitized Vapor Phase Photolysis of Perfluoro-1,6-heptadiene. Degassed perfluoro-1,6-heptadiene (50 mg, 0.160 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 2.5 days. On a vacuum line the volatile products were dynamically transferred into a U-trap (30 mg). Some high boiling material (polymeric residue) was found in the flask. ^{19}F NMR indicated the presence of *cis*- and *trans*-perfluorobicyclo[3.2.0]heptane as well as perfluorobicyclo[3.1.1]heptane (60% total yield), in the ratio 5.7:1.0:2.8. *trans*-Perfluorobicyclo[3.2.0]heptane. ^{19}F NMR : subsplit apparent AB quartet at −115.9, −123.4 (J = 217 Hz, 4F, C_2, C_4 or C_6, C_7), −116.2 (s, 2F, C_3), subsplit apparent AB quartet at −120.3, −125.4 (J = 223 Hz, 4F, C_6, C_7 or C_2, C_4), −188.0 (s, 2F, C_1, C_5). MS *m/e*: 312 (M^+, $C_7F_{12}^+$), 293 ($C_7F_{11}^+$), 243 ($C_6F_9^+$), 224 ($C_6F_8^+$), 212 ($C_5F_8^+$), 193 ($C_5F_7^+$), 181 ($C_4F_7^+$), 162 ($C_4F_6^+$), 143 ($C_4F_5^+$), 131 ($C_3F_5^+$, base), 124 ($C_4F_4^+$), 100 ($C_2F_4^+$), 93 ($C_3F_3^+$), 69 (CF_3^+). The photoreaction was also performed in the presence of nitrogen as a bath gas. Nitrogen (560 Torr) was introduced into the reaction flask after addition of the diene and a drop of Hg. Subsequent procedure was the same as above. ^{19}F NMR again revealed *cis*- and *trans*-perfluorobicyclo[3.2.0]heptanes and the [3.1.1] isomer, now in the ratio 3.6:1.0:1.1 (total yield 38 mg, 76%).

Direct Vapor Phase Photolysis of Perfluoro-1,6-heptadiene. As described above, the degassed diene (40 mg, 0.13 mmol) was transferred into an evacuated 150 mL quartz round-bottom flask, which was positioned as close as possible to the quartz cooling jacket surrounding an unfiltered 450 W medium pressure Canrad-Hanovia mercury lamp. The diene was irradiated for 2 days. When a vacuum transfer was attempted, no volatile products were found; the starting diene had completely polymerized.

Bromination of Perfluoro-1,6-heptadiene. A 25 mL three-necked flask fitted with a stirring bar, thermometer, reflux condenser, and dropping funnel was charged with a solution of 1 g of perfluoro-1,6-heptadiene (3.2 mmoL) in 10 mL of CCl_4. The flask was then cooled to 5 °C in an ice bath, and bromine was introduced dropwise under irradiation with a 150 W tungsten lamp until the bromine color persisted. Solvent was removed by distillation, and the product mixture was analyzed by ^{19}F NMR. No starting material remained; the product consisted almost entirely of cyclic dibromides **16** and acyclic tetrabromides **17** in the approximate ratio 65:35. The dibromides (cis/trans ratio, 2:1) and tetrabromides (meso/dl ratio, 1:1) were each purified by preparative GC. *cis*-Perfluorobis(bromomethyl)cyclopentane. ^{19}F NMR: AB quartet at −52.6, −57.8 (J = 211 Hz, 4F, *gem* to Br), AB quartet at −122.6, -125.2 (J = 266 Hz, 4F, C_3, C_5), AX quartet at −123.6, −133.2 (J = 250 Hz, 2F, C_4), -166.8 (s, 2F, C_1, C_2). *trans*-Perfluorobis(bromomethyl)cyclopentane. ^{19}F NMR: AB quartet at −52.6, −55.9 (J = 203 Hz, 4F, *gem* to Br), subsplit AB quartet at −124.5, −125.7 (J = 262 Hz, 4F, C_3, C_5), −131.1 (s, 2F, C_4), −172.0 (s, 2F, C_1, C_2). MS for cis-trans mixture, *m/e*: 470, 472, 474 (M^+), 391,393 ($C_7F_{12}Br^+$), 303, 305 (C_6F_8-Br^+), 243 ($C_6F_9^+$), 193 ($C_5F_7^+$), 181 ($C_4F_7^+$), 131 ($C_3F_5^+$), 69 (CF_3^+). Perfluoro-1,2,6,7-tetrabromoheptane. ^{19}F NMR: −57.2 (s, 4F, C_1, C_7) for both isomers, AB quartet at −110.3, −111.7 (J = 297 Hz, 4F, C_3, C_5) for dl or meso; AB quartet at −110.7, −111.6 (J = 297 Hz, 4F, C_3, C_5) for meso or *dl*; AB quartet at −114.1, −118.1 (J = 290 Hz, 2F, C_4) for meso; −116.2 (s, 2F, C_4) for *dl*; −131.0 (narrow m, 2F, C_2, C_6) for both.

The bromination was repeated at higher dilution. Into a 100 mL three-necked flask was placed 0.5 g (1.6 mmol) of perfluoro-1,6-heptadiene and 25 mL of CCl_4, and the flask was cooled to 5°C. A solution of bromine (0.25 g, 1.6 mmol) in 20 mL CCl_4 was slowly introduced dropwise with stirring under irradiation with the sunlamp. After 3 h reaction was complete, and solvent was removed by distillation. Analysis by ^{19}F NMR revealed the product to be the dibromides **16**, contaminated with only a very small amount of tetrabromides **17** and other impurities.

4,6,7-Trichloroperfluoro-1-heptene (26). This preparation was based on Fearn's procedure.[7] 3,5,7,8-Tetrachloroperfluorooctanic acid (10.0 g, 0.021 mol) was slowly added to 5 N aqueous NaOH solution. The mixture was carefully adjusted to pH 7. The solution was evaporated to dryness in a vacuum desiccator at 1 Torr overnight, yielding the sodium salt as a white solid (100% yield). The dry salt was pyrolyzed at ~300 °C and 1 Torr in a glass tube connected to a liquid nitrogen trap. Pyrolysis proceeded rapidly and smoothly, yielding crude monoalkene in the trap. When the trap contents were warmed CO_2 started bubbling out. The crude product was purified by a vacuum transfer, which gave 6.9 g (85%) of 95% pure 4,6,7-trichloroperfluoroheptene.

***cis*- and *trans*-Perfluoro-1,3,6-heptatriene (19 and 20). (a) Using Zinc in Ethanol.** A 50 mL three-necked flask was equipped with a mechanical stirrer, reflux condenser, and dropping funnel. A mixture of 20 mL of absolute ethanol and 2.5 g of activated zinc was gently heated at 50 °C with stirring. To this mixture was added 2.5 g (6.4 mmol) of 4,6,7-trichloroperfluoro-1-heptene with continued stirring. Heating was increased until refluxing was observed, and gentle reflux was maintained for 3−4 h. The reaction flask was cooled to room temperature and then equipped for distillation. Two liquid layers were observed in the receiving flask when the mixture was distilled. The bottom layer was the dehalogenated products, and the top was primarily the solvent ethanol. The top layer was diluted with water to drive out any fluorocarbons, and the combined yield of fluorocarbons was 1.8 g. By ^{19}F NMR analysis this mixture contained both *cis*- and *trans*-perfluoro-1,3,6-heptatriene as the major products in the ratio 1:1 (1.4 g, 79% yield); small amounts of 4-chloroperfluoro-1,6-heptadiene (0.25 g, 12%) and 4*H*-perfluoro-1,6-heptadiene (0.11g, 6%) were also present. The mixture was separated by preparative GC. *cis*-Perfluoro-1,3,6-heptatriene. ^{19}F NMR: −89.6 (m, 2F, C_1, C_7, cis to F), −105.8 (m, 2F, C_1, C_7, trans to F), −107.7 (m, 2F, C_5), −127.3 (d, J = ~31 Hz, 1F, C_3), −137.1 (narrow m, 1F, C_4), −177.9 (dt, J = 118 Hz, 39 Hz, 1F, C_2), −189.5 (ddt, J = 117 Hz, 39 Hz, 16 Hz, 1F, C_6). IR: 1781 (vs), 1711 (m), 1354 (s), 1322 (vs), 1285 (m), 1183 (s), 1134 (s), 1061 (m), 1041 (m , 966 (m), 841 cm^{-1} (s). MS *m*/*e*: 274 (M^+), 255 ($C_7F_9^+$), 224 ($C_6F_8^+$), 205 ($C_6F_7^+$, base), 186 ($C_6F_6^+$), 155 ($C_5F_5^+$), 131 ($C_3F_5^+$), 93 ($C_3F_3^+$), 69 (CF_3^+). *trans*-Perfluoro-1,3,6-heptatriene. ^{19}F NMR: −90.3 (m, 2F, C_1, C_7, cis to F), −103.5 (m, 1F, C_1, trans to F), −106.3 (m, 1F, C_7, trans to F), −106.2 (s, 2F, C_5), a subsplit AB quartet at −153.6, −154.7 (J = 140 Hz, 2F, C_3, C_4), −186.2 (m, 1F, C_2), −189.3 (m, 1 F, C_6). IR: 1783 (s), 1770 (s), 1710 (m), 1351 (m), 1333 (s), 1306 (s), 1268 (s), 1189 (s), 1063 (m), 974 (w) 820 cm^{-1} (w). MS *m*/*e*: 274 (M^+), 255 ($C_7F_9^+$), 243 ($C_6F_9^+$), 224 ($C_6F_8^+$), 205 ($C_6F_7^+$, base), 186 ($C_6F_6^+$), 155 ($C_5F_5^+$), 131 ($C_3F_5^+$), 93 ($C_3F_3^+$), 69 (CF_3^+). 4*H*-Perfluoro-1,6-heptadiene. ^{19}F NMR: −90.1 (m, 2F, C_1, C_7, cis to F), −106.1 (m, 2F, C_1, C_7, trans to F), subsplit apparent AB quartet at −111.4, −118.0 (J_{app} = 254 Hz, 4F, C_3, C_5), −189.9 (m, 2 F, C_2, C_6), −210.7 (d, 1F, C_4). 4-Chloroperfluoro-1,6-heptadiene. ^{19}F NMR −88.9 (dd, J = 47 Hz, 47 Hz, 2F, C_1, C_7, cis to F), −104.6 (m, 2F, C_1, C_7, trans to F), subsplit apparent AB quartet at −112.1, −113.4 (J_{app} = 289 Hz, 4F, C_3, C_5), −138.1 (s, 1F, C_4), −185.9 (m, 2F, C_2, C_6).

(b) Using Zinc in Diglyme. As described above, a mixture of 80 mL of absolute diglyme and 10.0 g of activated zinc was gently heated at 60 °C with stirring. To this mixture was added a small amount of 4,6,7-trichloroperfluorohept-1-ene with continued stirring, and heating was increased until the reaction began at about 100 °C. It started vigorously, and the rest of the alkene (total of 10.0 g, 0.026 mol) was slowly added to the mixture (~20 min), which was allowed to reflux for 8 h at 120−130 °C. After the mixture was cooled to room temperature, the reaction flask was equipped for distillation and the reaction products were distilled at atmospheric pressure. These products were separated from one another by preparative GC. Perfluoro-3-allylcyclobutene was the major product (4.27 g, 60%), accompanied by *trans*-perfluoro-1,3,6-heptatriene (2.00 g, 28%) and perfluorobicyclo[3.1.1]hept-2-ene (0.28 g, 4% yield).

Equilibration of the Trienes. *cis*-Perfluoro-1,3,6-heptatriene (15 mg, 0.054 mmol) and a catalytic amount of iodine were dissolved in $CDCl_3$; the solution was transferred to a NMR tube. The tube was well sealed, positioned in a cooling jacket, and irradiated by a tungsten lamp at 14 °C until no further changes occurred in the ^{19}F NMR spectrum. Equilibrium was reached after about 7 h, and the ratio of cis to trans triene was measured by multiple ^{19}F NMR integrations ($K_{c/t}$ = 1.67).

Perfluorobicyclo[3.1.1]heptene (28). A heavy-walled Pyrex ampule containing 0.10 g (0.37 mmol) of *cis*-perfluoro-1,3,6-heptatriene was pyrolyzed at 300 °C for 16 h; the tube was cracked open after cooling with liquid nitrogen, giving a clear colorless liquid. Its ^{19}F NMR spectrum showed that the starting triene had reacted completely, giving perfluorobicyclo[3.1.1]heptene in 100% yield. ^{19}F NMR: −115.0 (s, 2 F, C_4), subsplit apparent AB quartet at −129.9, −131.8 (J = 211 Hz, 4F, C_6, C_7), −144.1 (s, 1F, C_2), −162.3 (s, 1F, C_3), −215.4 (s, 1F, C_1 or C_4), −215.5 (s, 1F, C_4 or C_1). IR: 1743 (m), 1410 (w), 1364 (m), 1332 (m), 1276 (vs), 1201 (s), 1108 (m), 970 (s), 948 cm^{-1} (m). MS *m*/*e*: 274 (M^+), 255 ($C_7F_9^+$), 243 ($C_6F_9^+$), 224 ($C_6F_8^+$), 205 ($C_6F_7^+$, base), 186 ($C_6F_6^+$), 155 ($C_5F_5^+$), 131 ($C_3F_5^+$), 93 ($C_3F_3^+$), 69 (CF_3^+). HRMS *m*/*e*: 273.9844 (theor 273.9840). Pyrolysis of perfluoro-1,3,6-heptatriene was also performed at 250 °C for 22 h as described above, again giving perfluorobicyclo[3.1.1]heptene in 100% yield.

Perfluoro-3-allylcyclobutene (27). *cis*-Perfluoro-1,3,6-heptatriene (45 mg, 0.16 mmol) was transferred into a well-dried ampule and pyrolyzed at 134 °C for 22 h as described before. The ^{19}F NMR spectrum revealed perfluoro-3-allylcyclobutene accompanied by perfluorobicyclo[3.1.1]heptane in the ratio 14:1 (100% yield). Perfluoro-3-allylcyclobutene was purified by preparative GC. Perfluoro-3-allylcyclobutene. ^{19}F NMR: −89.6 (m, 1F, $C_{3'}$, cis to F), −106.0 (m, 1F, $C_{3'}$, trans to F), subsplit AB quartet at −109.9, −112.7 (J = 297 Hz, 2F, $C_{1'}$), subsplit AB quartet at -114.7, −116.6 (J = 195 Hz, 2F, C_4), −122.3 (s, 1F, C_1), −124.5 (s, 1F, C_2), −172.5 (s, 1F, C_3), −191.1 (m, 1 F, $C_{2'}$). IR: 1783 (vs), 1394 (vs), 1357 (m), 1345 (m), 1312 (s), 1186 (vs), 1155 (vs), 1115 (m), 1070 (s), 953 (m), 855 (m), 805 cm^{-1} (m) . MS *m*/*e*: 274 (M^+), 255 ($C_7F_9^+$), 243 ($C_6F_9^+$), 224 ($C_6F_8^+$), 205 ($C_6F_7^+$), 186 ($C_6F_6^+$), 155 ($C_5F_5^+$), 131 ($C_3F_5^+$, base), 93 ($C_3F_3^+$), 69 (CF_3^+). HRMS *m*/*e*: 273.9842 (theor 273.9840). When pyrolysis of *cis*-perfluoro-1,3,6-heptatriene was carried out at 200 °C for 24 h, the starting triene was completely converted to perfluoro-3-allylcyclobutene and perfluorobicyclo[3.1.1]heptene, now in the ratio 1:1.

Pyrolysis of *trans*-Perfluoro-1,3,6-heptatriene. A heavy-walled Pyrex ampule containing 50 mg (0.18 mmol) of pure *trans*-perfluoro-1,3,6-heptatriene was heated at 133 °C for 24 h. The ^{19}F NMR spectrum showed only starting triene. The same result was obtained after heating for 25 h at 181 °C. However, when the triene was pyrolyzed at 250 °C for 20 h, perfluorobicyclo[3.1.1]heptene was formed in 50% yield (25 mg), together with polymer.

Conversion of *trans*-Perfluoro-1,3,6-heptatriene to Perfluoro-3-allylcyclobutene. As described above, a mixture of 45 mg (0.16 mmol) of pure *trans*-perfluoro-1,3,6-heptatriene and a catalytic amount of I_2 was subjected to pyrolysis at 130 °C for 24 h. The ^{19}F NMR spectrum of the product revealed perfluoro-3-allylcyclobutene accompanied by perfluorobicyclo[3.1.1]heptene in the ratio 14:1.

Pyrolysis of Perfluoro-3-allylcyclobutene. A 35 mg (0.13 mmol) sample of pure perfluoro-3-allylcyclobutene was pyrolyzed at 250 °C for 24 h; the ^{19}F NMR spectrum demonstrated that the starting material had entirely disappeared and perfluorobicyclo[3.1.1]heptane had formed as the only product.

Mercury-Sensitized Vapor-Phase Photolysis of Perfluoro-3-allylcyclobutene. Degassed perfluoro-3-allylcyclobutene (42 mg, 0.15 mmol) was transferred into an evacuated 150 mL quartz round-bottom flask fitted with a stopcock and containing a drop of mercury. The sample rapidly vaporized when warmed to room temperature. The flask was centered in the cavity photoreactor and irradiated for 18 h at about 37 °C. After photolysis, the volatiles were dynamically transferred into a U-trap (16 mg) on a vacuum line. High boiling material (polymeric residue) was found in the flask. ^{19}F NMR revealed the presence of perfluorotricyclo[2.1.1.0^{2,5}]heptane in the volatile fraction. In order to isolate this fluorocarbon the photolysis was repeated in a cylindrical 3 L quartz flask. The flask, containing two drops of mercury, was fitted with a stopcock and evacuated (15 mTorr). It was cooled to 0−5 °C in an ice bucket. The short extension of the stopcock was sealed with a septum, and perfluoro-3-allylcyclobutene (0.35 g, 1.28 mmol) was injected into this tube. Now the stopcock was opened briefly to allow the sample to vaporize and pass into the chamber. The flask was shaken to spread the mercury over its wall in small droplets. It was positioned in the cavity photoreactor and irradiated for 2 days. After photolysis, the volatile products were transferred into a U-trap (0.15 g) on a vacuum line. Perfluorotricyclo[2.2.1.0^{2,5}]heptane was purified by preparative GC (38 mg, 11% yield). ^{19}F NMR: subsplit AB quartet at −104.3, −134.6 (J = 188 Hz, 4F, C_3, C_6), -125.2 (t, J = 23 Hz, 2F, C_7), −213.8 (s, 2F, C_1, C_4 or C_2, C_5), −215.5 (s, 2F, C_2, C_5 or C_1, C_4). IR: 1414 (m), 1369 (m), 1324 (m), 1305 (s), 1288 (m), 1240 (s), 1212 (m), 1170 (w), 995 (m), 954 (m), 863 cm^{-1} (m). MS *m/e*: 274 (M^+), 255 ($C_7F_9^+$), 243 ($C_6F_9^+$), 224 ($C_6F_8^+$), 205 ($C_6F_7^+$, base), 186 ($C_6F_6^+$), 174 ($C_5F_6^+$), 155 ($C_5F_5^+$), 131 ($C_3F_5^+$), 124 ($C_4F_4^+$), 105 ($C_4F_3^+$, 93 ($C_3F_3^+$), 69 (CF_3^+). HRMS *m/e*: 273.9838 (theor 273.9840). This isomer was accompanied by a small amount of perfluorotricyclo[3.1.1.0^{3,6}]heptane, as judged from its ^{19}F NMR spectrum: −113.6 (d, J = 219 Hz, 3F, C_2, C_4, C_7), −138.1 (d, 219 Hz, 3F, C_2, C_4, C_7), −203.4 (subsplit d, J = 39 Hz, 3F, C_1, C_3, C_5), −217.0 (1F, C_6).

Mercury-Sensitized Vapor Phase Photolysis of *cis*-Perfluoro-1,3,6-heptatriene. Degassed *cis*-perfluoro-1,3,6-heptatriene was transferred into an evacuated 150 mL quartz round-bottom flask fitted with a stopcock and containing a drop of mercury. The flask was irradiated for 18 h at ~37 °C, after which its volatile contents were transferred into a U-trap on a vacuum line. The ^{19}F NMR spectrum showed a mixture similar to that obtained from photolysis of perfluoro-3-allylcyclobutene. Perfluorotricyclo[2.2.1.0^{2,5}]heptane was obtained in 12% yield. *trans*-Perfluoro-1,3,6-heptatriene was also irradiated in the presence of Hg for 18 h at ~37 °C as described above. The ^{19}F NMR spectrum of the volatile fraction was similar to that obtained with the cis isomer.

Direct Vapor Phase Photolysis of *cis*-Perfluoro-1,3,6-heptatriene. Degassed triene (42 mg, 0.15 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 an unfiltered 450 W medium pressure Canrad-Hanovia mercury lamp, and the triene was photolyzed for 18 h. When the volatile product was transferred into a U-trap (40 mg, 95%), no high boiling material was observed in the flask. The ^{19}F NMR spectrum of the clear, colorless liquid showed that the starting triene had reacted completely and perfluoro-3-allycyclobutene was the sole product.

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