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Interrelationships among C_6F_{10} Valence Isomers[1]

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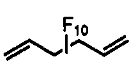
Thermal and photochemical interconversions among the three valence isomers perfluoro-1,5-hexadiene (1), perfluorobicyclo[2.2.0]hexane (2), and perfluorobicyclo[2.1.1]hexane (3) have been explored. At 250 °C 1 and 2 exist in equilibrium with $K_{1\to2} = 1.1$, but at higher temperatures irreversible isomerization to 3 becomes rapid. This chemistry contrasts sharply with the behavior of the corresponding hydrocarbons, where the diene is lowest in free energy. Mercury-sensitized photolysis of diene 1 yields 3 and 2 in ratios of 3–4:1. The cleanness of both the thermal and the photochemistry, together with thermodynamics favorable to cyclization, bode well for synthesizing new bicyclic and polycyclic fluorocarbons from other unsaturated precursors.

Fluorocarbons, as a rule, differ markedly in chemical behavior from their hydrocarbon counterparts, and the study described here of thermal and photochemical valence isomerizations in a simple fluorocarbon system has yielded results true to this expectation. Our findings also suggest how one might take advantage of thermodynamic differences between fluorocarbons and hydrocarbons in synthetic approaches without parallel in hydrocarbon chemistry to a variety of bi- and polycyclic fluorocarbons that are presently unknown or accessible only with difficulty. We have examined the interplay among three C_6F_{10} valence isomers: perfluoro-1,5-hexadiene (1), perfluorobicyclo[2.2.0]hexane (2), and perfluorobicyclo[2.1.1]hexane (3).



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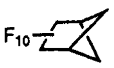

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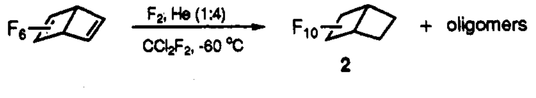
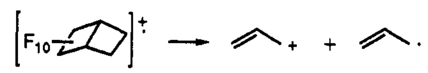
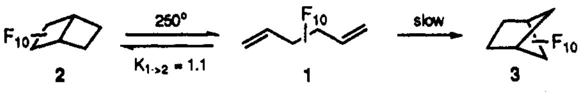
The work began with synthesis of isomer 2, which had been obtained previously in 2% yield as a byproduct in the reaction of perfluorodewarbenzene with bis(fluoroxy)difluoromethane.[2] Direct fluorination of the dewarbenzene, which is prepared in >90% yield by photolysis of perfluorobenzene,[3,4] with elemental fluorine in helium gave 2 in 30–35% yields. The reaction was best carried out at low temperatures (−60 °C) in dichlorodifluoromethane (Freon 12).[5] Fluorocarbon 2 was identified by its ^{19}F NMR and mass spectra. The latter showed no parent peak but was dominated by a peak at *m/e* 131, just half of the parent mass. Thus, the molecular ion splits down the middle efficiently to yield an allyl radical and an allyl cation, a fragmentation pathway which has also been observed with the parent hydrocarbon[6] and other highly fluorinated bicyclo[2.2.0]hexanes.[7]





Fluorinated oligomers accounted for virtually all of the dewarbenzene which did not give 2. The infrared spectrum of this nonvolatile fraction was devoid of C═C and ═C·F stretching bands, so the oligomers were apparently saturated with fluorine. Whether the halogen be bromine, chlorine, or fluorine, addition to perfluorodewarbenzene presumably proceeds via a radical-chain mechanism, but with bromine and chlorine the reaction is very clean.[3,8] The contrast in the case of fluorine probably arises because the steady-state concentration of the halogen during the reaction is low, thus allowing C–C double bonds to compete effectively with elemental fluorine for the carbon radicals formed during fluorination.

Heating bicyclic fluorocarbon 2 in quartz ampules at 200 °C had no effect, but at 250 °C diene 1[9] was slowly formed, as determined by ^{19}F NMR. Progress ceased when slightly less than half of the starting material had been transformed. That equilibrium between the two isomers had been achieved was demonstrated by heating a sample of purified 1 and observing its cyclization to 2. Measurements carried out after heating 2 for many half-lives ($t_{1/2}$ = 13 h) established that $K_{1\to2} = 1.1$ at 250 °C. At 300 °C, the equilibrium constant was found to be substantially smaller; therefore, the enthalpy content of 1 is higher than that of 2. From the fact that its free energy is very close to that of 2 at these temperatures it follows that 1 must also have the higher entropy content, as would be anticipated just from considerations of symmetry and rigidity.



During the equilibration process a new set of ^{19}F NMR signals very slowly emerged from the base line, signals arising from the bicyclo[2.1.1] valence isomer 3. Only a few percent of 3 had formed after 80 h. The NMR

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[1] This work was presented in part at the 12th International Symposium on Fluorine Chemistry, University of California, Santa Cruz, CA, Aug 1988.

[2] Toy, M. S.; Stringham, R. S. *J. Fluorine Chem.* **1978**, *13*, 23.

[3] Camaggi, G.; Gozzo, F. *J. Chem. Soc. C* **1969**, 489.

[4] Dailey, W. P.; Correa, R. A.; Harrison, E. H., III; Lemal, D. M. *J. Org. Chem.* **1989**, *54*, 5511.

[5] Fluorination was much faster in dichlorodifluoromethane than in either trichlorofluoromethane or 1,2-dichlorotetrafluoroethane, and much less polymer was formed. The more dilute the solution the less polymer was produced, but this effect was not dramatic.

[6] Srinivasan, R. *J. Am. Chem. Soc.* **1961**, *83*, 4923.

[7] Correa, R. A. Ph.D. Dissertation, Dartmouth College, 1990.

[8] Barlow, M. G.; Haszeldine, R. N.; Morton, W. D.; Woodward, D. R. *J. Chem. Soc., Perkin Trans. I* **1972**, 2170.

[9] Fainberg, A. H.; Miller, W. T. *J. Am. Chem. Soc.* **1957**, *79*, 4170.

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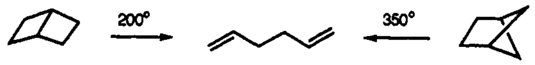
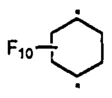
resonances comprised a triplet at 127.8 ppm (J_{app} = 20 Hz) for the C_2-bridge fluorines, an apparent (subsplit) AB quartet at 121.8 and 137.8 ppm (J_{app} = 208 Hz) for the C_1-bridge fluorines, and a triplet at 222.5 ppm (J_{app} = 7 Hz) for the bridgehead fluorines. Pyrolysis of 2 at 350 °C for 12 h gave 3 exclusively, reflecting the smaller ring strain in the [2.1.1] relative to the [2.2.0] isomer.[10] It is noteworthy that the interconversions of isomers 1-3 were very clean under all of the conditions explored.

Long ago, Fainberg and Miller[9] pyrolyzed 1 and obtained a product to which they assigned structure 2. Their compound was in fact 3, and they did not find valence isomer 2. The mistake in structure assignment is not at all surprising, as this work was done before ^{19}F NMR had become available.

Interestingly, the thermodynamic relationship between the diene and its bicyclic valence isomers is very different in the hydrocarbon series. Srinivasan prepared and studied the pyrolysis of both bicyclo[2.2.0]hexane[11] and bicyclo[2.1.1]hexane.[12] In each case ring opening to the hexadiene was complete. Relief of ring strain augmented by an increase in entropy content sufficed to drive these reactions all the way. The fact that the very strained 2 is comparable in free energy to 1 at 250 °C and that 3 is distinctly lower in free energy than 1 reflects the well-known driving force for highly fluorinated double bonds to become saturated.[13] At least two factors contribute to that driving force. Fluorine substituents favor a change from sp^2 to sp^3 hybridization because of their high electronegativity, and lone pair–π repulsion further destabilizes heavily fluorinated double bonds.



The lower activation energy for the formation of 2 than for 3 despite the greater thermodynamic stability of the latter is understandable when the reaction mechanism is considered. Both products are formally the result of an internal [2 + 2] cycloaddition, and as such their formation in concerted fashion is orbital topology-forbidden.[14] Undoubtedly, 2 arises via biradical 4 and 3 via 5.[15] Preferential formation of biradical 4 can be rationalized on the basis of its smaller ring strain;[16] i.e., it is in the second step of the reaction leading to 2 and 3, cyclization of the biradical, that 2 acquires the greater strain energy.[17]



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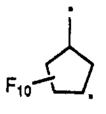

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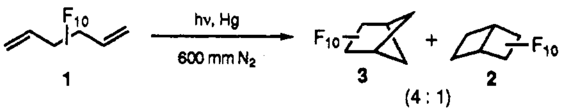
Table I. Mercury-Sensitized Vapor-Phase Photolysis of Perfluoro-1,5-hexadiene (1)[a]

diene 1 (g)	irradn time (h)	yield of 3 (%)	yield of 2 (%)	recovery of 1 (%)	polymers (%)
0.19	4	43	12	38	7
0.20	12.5	53	16	23	8
0.19	38	63	15	9	13
0.15	48	60	20	0	20
0.20[b]	4	17	4	77	2
0.14[b]	38	66	17	0	17

[a] Yields based on ^{19}F NMR (282.2 MHz) integration. [b] Nitrogen (600 mm) added.

The photochemistry of diene 1 was also explored. Direct irradiation with an unfiltered medium-pressure mercury arc in the vapor phase led only to polymeric material, even when nitrogen (600 mm) was present as a buffer gas.



In contrast, mercury sensitization in the vapor phase with 2537-Å radiation gave high yields of 2 and 3, in ratios of 1:3–4, accompanied by relatively small amounts of polymer (Table I). The product composition was essentially the same when the sensitized reaction was performed in the presence of 600 mm of nitrogen to assure rapid collisional cooling of vibrationally hot species. It is interesting that the bicyclic isomer which is more easily formed in the thermal chemistry of diene 1 is the minor product photochemically. Again, the experimental finding can be explained in terms of the relative ease of formation of biradicals 4 and 5. In the photoreaction those biradicals are presumably generated as triplets,[18] not singlets as in the ground-state reaction, but that is probably not an important difference. The transition states for biradical formation should, according to the Hammond postulate,[19] come very early in the triplet state reaction since the biradical lies far below the triplet state of 1 in energy by virtue of its new C–C bond. Thus, the relative stability of the biradicals is not very important, as it is in the ground state where the Hammond postulate dictates a late transition state, and stereoelectronic considerations dominate the choice of pathways in the triplet-state reaction (Figure 1). If one accepts 6 as an appropriate, albeit oversimplified, representation of the T_1 state of the diene, cyclization to 5 should be preferred over 4 for the same reason that 5-hexenyl radicals cyclize to cyclopentylcarbinyl radicals instead of cyclohexyl radicals; namely, because favorable geometry for creation of the new C–C bond is achieved with less ring strain.[20]

The cleanness with which perfluoro-1,5-hexadiene cyclizes both thermally and photochemically bodes well for

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[10] The difference in strain energy for the parent hydrocarbons is about 9.5 kcal/mol. Greenberg, A.; Liebman, J. F. *Strained Organic Molecules*; Academic Press: New York, 1978; p 72.

[11] Steel, C.; Zand, R.; Hurwitz, P.; Cohen, S. G. *J. Am. Chem. Soc.* **1964**, *86*, 679.

[12] Srinivasan, R.; Levi, A. A. *J. Am. Chem. Soc.* **1963**, *85*, 3363.

[13] The thermodynamics of fluorine substitution at unsaturated and saturated carbon is discussed in: Smart, B. E. *Mol. Struct. Energ.* **1986**, *3*, 141.

[14] Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781.

[15] Alkenes having geminal fluorines readily undergo cycloadditions via biradicals. Bartlett, P. D.; Hummel, K.; Elliott, S. P.; Minns, R. H. *J. Am. Chem. Soc.* **1972**, *94*, 2898 and references cited therein.

[16] The fact that 4 is disecondary may be no advantage since these are *fluorocarbon* biradicals; BDE(CF_3CF_2-H) and BDE($(CF_3)_2CF$-H) are the same within experimental error (ref 13).

[17] Attempts were made to trap the short-lived 1,4-cyclohexanediyl by hydrogen atom donation. Diene 1 was heated at temperatures up to 220 °C with 1,3,5-triisopropylbenzene, but only starting material and 2 were detected by ^{19}F NMR.

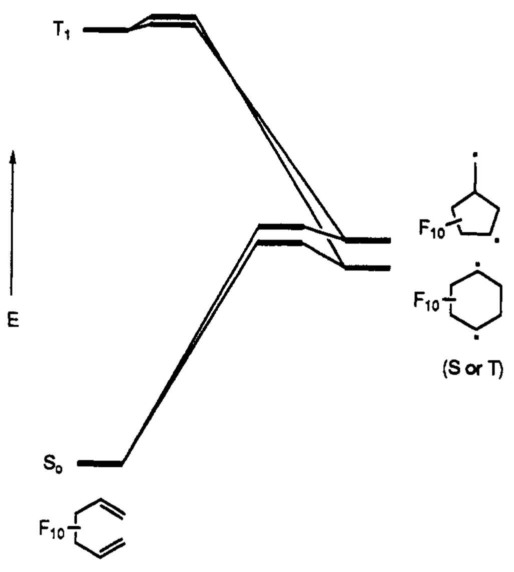
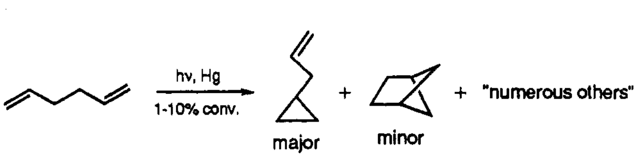


Figure 1. Schematic representation of biradical formation from diene 1 in the ground and lowest triplet states.

the synthesis of a variety of highly fluorinated bicyclic and polycyclic ring systems by cyclization of diene and polyene precursors. This prospect is the more significiant in light of the fact that alternative synthetic methodology for assembling such fluorocarbon skeletons is extremely limited at the present time.[21] Much of the anticipated chemistry will be without parallel among the corresponding hydrocarbons, both because of the thermodynamic differences discussed above and for kinetic reasons. By the latter we refer to differences in reactivity between C–H and C–F bonds which can make the hydrocarbon chemistry complex and messy in cases where fluorocarbons react cleanly. Hydrogen atoms bound to carbon are readily abstracted by free radicals while the more tightly bound fluorine atoms are not, and hydrogen atoms undergo shifts much more readily than fluorines. The point is nicely illustrated by the photochemistry of 1,5-hexadiene, studied by Srinivasan.[22] In contrast to the cyclization of 1, the parent hydrocarbon upon mercury sensitization yields even at conversions of only 1–10% a complex array of products among which just allylcyclopropane and bicyclo[2.1.1]-hexane have been identified.



We are currently exploring the thermal and photochemistry of other perfluoro dienes and trienes in order both to discover ground rules governing their modes of cyclization and to synthesize new bi- and polycyclic fluorocarbons.

Experimental Section

General Procedures. ^{19}F NMR spectra were recorded 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 upfield from internal $CFCl_3$. Infrared spectra were measured on a Perkin-Elmer 599 spectrophotometer. Mass spectra were determined on a Finnigan 4023 quadrupole mass spectrometer. Analytical GC was carried out with a Hewlett-Packard 5880A gas chromatograph equipped with a flame ionization detector. Peak areas were determined by electronic integration, and they are uncorrected for differential detector response. Yields are corrected for purity as judged by GC. Preparative GC separations were performed on a Hewlett-Packard 5750 gas chromatograph. 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 an unfiltered 450-Watt 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.[23] Zinc was activated according to the procedure of Shriner and Newman.[24] Ethylene glycol dimethyl ether was distilled from lithium aluminum hydride. Dioxane was purified over Na and then distilled. Hexafluorodewarbenzene was prepared by irradiation of hexafluorobenzene (Fairfield).[3,4] Perfluoroallyl fluorosulfate was synthesized by the reaction of sulfur trioxide (Aldrich) with perfluoropropene (PCR).[25] Perfluoroallyl iodide was prepared from the fluorosulfate[25] and then coupled according to Miller's procedure to give perflluoro-1,5-hexadiene.[9] The diene was purified by preparative GC.

Perfluorobicyclo[2.2.0]hexane (2). A solution of hexafluorodewarbenzene (90%, with 10% hexafluorobenzene; 0.093 mol) in dichlorodifluoromethane (400 mL) was placed in a precooled (−78 °C) 500-mL heavy-walled cylindrical reactor. Fluorination (F_2/He, 20:80, 45 cc/min) was carried out for 3 h at −60 °C; completion of the reaction was indicated by ^{19}F NMR. [The reaction can be run between −45 and −70 °C with the same results.] Argon was bubbled through the solution to flush out unreacted fluorine. The bulk of the solvent was evaporated through a −20 °C U-trap by allowing the reaction vessel to warm slowly to −5 °C, and the residual liquid was statically vacuum transferred into a 100-mL round-bottom flask and combined with the contents of the −20 °C trap. Remaining solvent was removed through a 60-cm jacketed distillation column packed with 3-mm glass beads. This column was maintained at −26 °C while the pot was slowly allowed to warm until refluxing ceased. Residual liquid was statically vacuum transferred into a U-trap containing phosphorus pentoxide to dry it and then vacuum transferred into a glass storage bulb, yield 8.2 g of 95% pure (by GC, 25-m methylsilicone capillary, 10 psi, 12 °C, t_R = 1.55 min) perfluorobicyclo[2.2.0]-hexane (32%). Solvent was the sole impurity. A total of 8.8 g of high molecular weight material was recovered, accounting for about 50% of the starting material. The bicyclohexane was obtained pure by preparative GC (25 ft × 1/8 in., 20% QF-1 on 80/100 mesh Chromosorb-W HP). ^{19}F NMR: subsplit apparent AB quartet at 118.9, 128.3 (J_{app} = 239 Hz, 8F, CF_2), 199.1 ppm (quintet, J_{app} = 6 Hz, 2F, CF). MS *m/e*: 193 ($C_5F_7^+$), 155 ($C_5F_5^+$), 143 ($C_4F_5^+$), 131 ($C_3F_5^+$, base), 100 ($C_2F_4^+$).

Thermolysis of Perfluorobicyclo[2.2.0]hexane (2). This experiment is representative of many that were carried out. Into a well-dried quartz ampule which had been evacuated to 0.01 Torr and cooled with liquid nitrogen was transferred 0.02 g (0.076 mmol) of 100% pure (by GC) perfluorobicyclo[2.2.0]hexane. The ampule was degassed by two freeze–pump–thaw cycles and sealed under vacuum. It was heated to 250± 2°C in a salt bath, and after 100 h it was removed from the bath and cooled with ice–water. The ampule was cracked open under vacuum, and its contents were transferred into an NMR tube containing 0.4 mL of $CDCl_3$. ^{19}F NMR revealed the presence of isomers 1, 2, and a small amount of 3. The ratio of 2 to 1 was 1.1:1, and this value was confirmed by GC. The three isomers were separated by preparative GC (QF-1, as above). ^{19}F NMR of 1: 88.3 (subsplit

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[18] Calvert, J. G.; Pitts, J. N., Jr. *Photochemistry*; John Wiley and Sons: New York, 1966; p 68 *et seq.*

[19] Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334.

[20] Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry*, 3rd ed.; Plenum Press: New York, 1990; Part A, p 678.

[21] In fact, fluorination of preformed hydrocarbon skeletons is the only general method available now for obtaining such compounds.

[22] Srinivasan, R. *J. Phys. Chem.* **1963**, *67*, 1337.

[23] Perrin, D. D.; Armaredo, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon Press: Oxford, 1980.

[24] Shriner, R. L.; Newman, R. W. *Organic. Syntheses;* Wiley: New York, 1955;Collect. Vol. III, p 73.

[25] Krespan, C. G.; Dixon, D. A. *J. Org. Chem.* **1986**, *51*, 4460.

t, 2F, cis terminal), 105.7 (m, 2F, trans terminal), 120.0 (narrow m, 4F, CF_2), 189.3 (subsplit d, 2F, internal vinyl). ^{19}F NMR of **3**: 127.8 (t, J_{app} = 20 Hz, 4F, C_2 bridge), subsplit apparent AB quartet at 121.8 and 137.8 (J_{app} = 208 Hz, 4F, C_1 bridges) and 222.5 ppm (t, J_{app} = 7 Hz, 2F, bridgeheads). IR (vapor) of **3**: 1370, 1290, 1260, 980, 960, 950 cm^{-1}. MS *m/e* of **3**: 193 ($C_5F_7^+$), 155 ($C_5F_5^+$), 143 ($C_4F_5^+$), 131 ($C_3F_5^+$, base).

Mercury-Sensitized Vapor-Phase Photolysis of Perfluoro-1,5-hexadiene (1). Degassed perfluoro-1,5-hexadiene (0.2 g) 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 photolyzed. On a vacuum line the reaction mixture was dynamically transferred into a U-trap. Some high-boiling material (polymeric residue) was found at the bottom of the flask. ^{19}F NMR indicated the presence of perfluorobicyclo[2.1.1]hexane (**3**) and its [2.2.0] isomer (**2**). Product yields and irradiation times are listed in Table I.

When the photolysis was repeated in a flask coated with polymer film from the previous run, conversion to **2** and **3** after 4 h was as high as in a clean flask, thus showing that the polymer did not inhibit the photochemistry. Photolyses were also carried out in the presence of nitrogen as a bath gas. Nitrogen (600 mm) was introduced into the reaction flask after addition of diene **1**, and the subsequent procedure was the same as above. Photolysis times and yields are given in Table I.

Direct Vapor-Phase Photolysis of Perfluoro-1,5-hexadiene (1). As described above, the diene (0.12 g) was transferred into an evacuted 250-mL quartz round-bottom flask. The flask was positioned as close as possible to the quartz cooling jacket surrounding an unfiltered 450-W Canrad-Hanovia medium-pressure mercury lamp. Irradiation was carried out for 26 h. When the reaction mixture was transferred into a U-trap, high-boiling material remained on the bottom of the flask. The ^{19}F NMR spectrum of the colorless liquid which transferred revealed only starting material (20% recovery). Neither compound **2** nor **3** was formed. The reaction was also performed in the presence of 600 mm of nitrogen gas, but only polymeric residue was found.

Acknowledgment. We thank the Air Force Office of Scientific Research and the National Science Foundation for support of this research.