small), 166.2 (1 F), 172.3 ppm (1 F).

Hexafluoro-2,4-cyclohexadienone (12). Vacuum flow pyrolysis of hydrate **4c** (0.811 g, 3.68 mmol) in a quartz tube at 300 °C and 0.1 mm gave a yellow liquid trapped at −196 °C. This product was dissolved in 20 mL of trichlorofluoromethane, dried over $MgSO_4$, gravity filtered, and distilled to give dienone **12**[6a] (0.66 g, 3.26 mmol, bp 115–119 °C) in 88% yield. [The weight of the starting material given above was determined by difference since about 10% of this unstable substance had remained behind as a nonvolatile brown residue.]

Hexafluorocyclopentadiene (13). Flash vacuum pyrolysis of hydrate **4c** (0.217 g, 0.986 mmol) at 0.1 mm in a tandem quartz hot tube (5 mm o.d., 45 cm at 350 °C, 50 cm at 600 °C) yielded a volatile product caught at −196 °C. Static vacuum transfer of this product gave hexafluorocyclopentadiene[4,6a] (0.137 g, 0.787 mmol, 80% yield) in about 95% purity as judged by ^{19}F NMR spectroscopy.

1-Chloropentafluorocyclopentadiene (33) and 2-Chloropentafluorocyclopentadiene (34). Flash vacuum pyrolysis of chloro ketone **3b** (41.6 mg, 0.190 mmol) at 650 °C (0.1 mm, 8 mm × 45 cm quartz tube) gave 17.3 mg of a volatile oil trapped at −196 °C. As shown by ^{19}F NMR analysis, this oil contained **33**, **34**,[3a,6a] and hexafluorobenzene in the ratio 2.3:1.0:0.15. The yield of cyclopentadienes was 47%.

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

5,6-Dichlorohexafluorocyclohexa-1,3-dienes: Hexafluorobenzene Synthons[1]

William P. Dailey, Ricardo A. Correa, Edwin Harrison, III, and David M. Lemal*

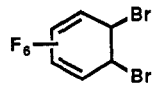
Department of Chemistry, Dartmouth College, Hanover, New Hampshire 03755

Received August 9, 1988

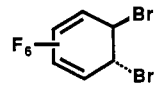
cis-5,6-Dichlorohexafluorocyclohexa-1,3-diene (*cis*-**8**) has been synthesized in five steps and 63% overall yield from hexafluorobenzene (**1**). Attempts to synthesize the bromine analogue of **8** have failed because aromatization occurs in the final, pyrolytic step. Conjugated diene *cis*-**8** rearranges at high temperatures with either chloride or fluoride migration to 1,4-cyclohexadienes. A 1:1 mixture of *cis*- and *trans*-**8** has been prepared from hexafluorobenzene in three steps. The trans isomer is reduced to **1** by iodide ion 16 ± 1 times faster than the cis isomer at 25 °C. These dienes undergo clean Diels–Alder addition to 4-phenyl-1,2,4-triazoline-3,5-dione at 110 °C, the trans isomer reacting 1.9 ± 0.1 times faster than the cis isomer. Dienes **8** are useful as reactive synthetic equivalents of hexafluorobenzene from which new unsaturated fluorocarbons can be fashioned.

Hexafluorobenzene (**1**) has spawned a large number of derivatives, most of which have been formed by nucleophilic attack upon the electron-deficient ring.[2] While this benzene is also capable of [2 + 2] photocycloaddition reactions, it is notably resistant to thermal cycloadditions of all types. Hoping to use **1** as a starting point for syntheses of higher perfluoroannulenes, perfluoroannulenium ions, and their valence isomers, we were particularly interested in carrying out cycloadditions on the hexafluorobenzene skeleton. Clearly, a synthon was required that would incorporate in regenerable fashion the elements of **1** but would be far more reactive. 5,6-Dihalohexafluoro-1,3-cyclohexadienes, e.g., dibromo dienes **2**, seemed to satisfy well these criteria for a synthon, offering as they do opportunities for both 1,2- and 1,4-cycloaddition reactions.

1



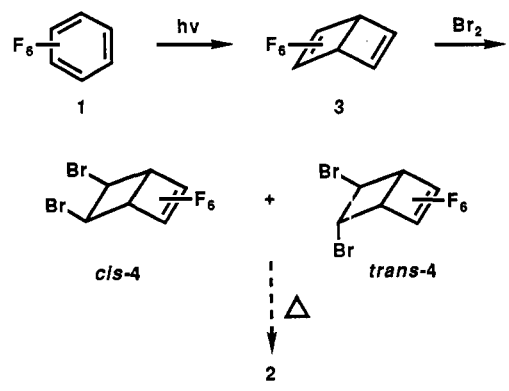
cis-**2**



trans-**2**

Either bromine or chlorine could serve the purpose of blocking a "double bond" of the benzene, but ease of subsequent reductive elimination made bromine the more attractive choice. Synthesis of **2** was therefore undertaken as shown in Scheme I. Dewar benzene **3**[3-5] was prepared by vapor-phase irradiation in 90% yield and, because of its tendency to detonate capriciously as a neat liquid, handled subsequently in solution only. It was brominated in trichlorofluoromethane (Freon 11) solution to give in 98% yield a 2:1 mixture of *cis*- and *trans*-**4**.[4,5] The orbital topology-forbidden thermal ring opening of **4** to **2** was not successful, however. When Pyrex ampules of neat **4** were heated to 160–180 °C for periods of 20 to 30 min, the only products were bromine and hexafluorobenzene (eq 1).

Scheme I



(1) This paper is based principally on the Ph.D. Dissertation of W. P.D., Dartmouth College, 1983.

(2) Smart, B. E. In *The Chemistry of Functional Groups, Supplement D: The Chemistry of Halides, Pseudohalides and Azides*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, 1983; Part I, pp 603–55. Hudlicky, M. *Chemistry of Organic Fluorine Compounds*, 2nd ed.; Halsted Press, Wiley: New York, 1976. Chambers, R. D. *Fluorine in Organic Chemistry*; Wiley: New York, 1973. Sheppard, W. A.; Sharts, C. M. *Organic Fluorine Chemistry*; Benjamin: New York, 1969.

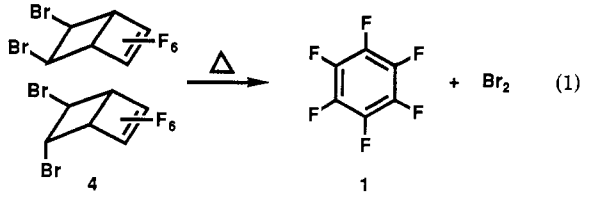
(3) Camaggi, G.; Gozzo, F.; Cevidalli, G. *J. Chem. Soc., Chem. Commun.* **1966**, 313–4. Haller, I. *J. Am. Chem. Soc.* **1966**, *88*, 2070–1.

(4) Camaggi, G.; Gozzo, F. *J. Chem. Soc. C* **1969**, 489–500.

(5) Barlow, M. G.; Haszeldine, R. N.; Morton, W. D.; Woodward, D. R. *J. Chem. Soc., Perkin Trans. I* **1972**, 2170–80.

0022-3263/89/1954-5511$01.50/0

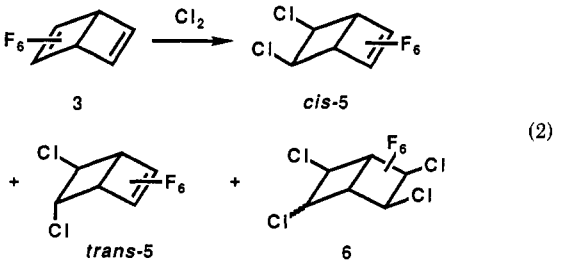
When the pyrolysis was attempted under flow conditions using a Pyrex-helix packed tube heated to 220 °C and evacuated to 14 Torr, the major products were once again bromine and 1.



(1)

Whether bromine elimination or ring opening is the first step in this transformation has not been proven, but the fact that it occurs under milder conditions than ring opening of the chloro analogues (see below) argues that bromine loss is the initial event for the bulk of the material. Bromine loss is probably initiated by ring opening of a trace of **4**, however. Homolysis of the activated C–Br bonds of the resulting **2** would yield bromine atoms that could initiate radical chain debromination of **4**. This process would be simply the reverse of the mechanism for radical chain bromination, with aromatization of the Dewar benzene product providing the driving force for bromine elimination.

The much greater strength of the carbon–chlorine relative to the carbon–bromine bond[6a] suggested that the same reaction sequence should be attempted with the former halogen. Chlorinating neat Dewar benzene **3** on a small scale, Barlow et al. have reported the preparation of dichlorides **5** in 90% yield.[5] In our hands the same reaction in Freon 11 solution in the dark proved to be much less selective, invariably giving substantial amounts of tetrachlorides and unreacted starting material in addition to the desired dichlorides (eq 2). Typically, the

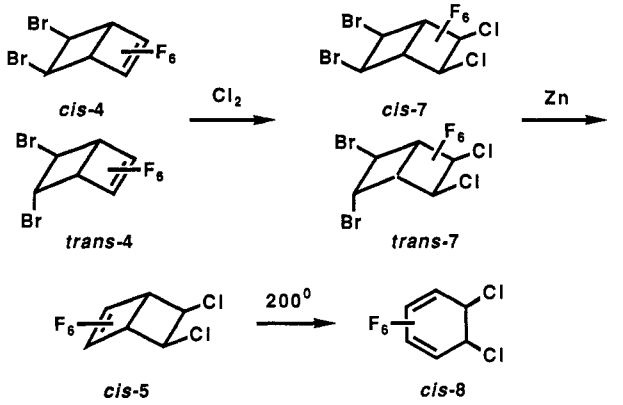


(2)

reaction yielded a 1:1 mixture of *cis*- and *trans*-**5** (55%) accompanied by unchanged **3** (15%) and 2,3,5,6-tetrachlorobicyclohexanes **6** (30%). Varying concentrations and temperature had little effect on the product ratios.

We hoped to be able to influence the cis/trans ratio of dichlorides and, more importantly, to minimize tetrachlorination by tempering the reactivity and/or increasing the effective bulk of the chlorine atoms that attack the fluorocarbon in this radical chain chlorination. Russell had demonstrated long ago that the selectivity of chlorine atoms in hydrogen abstraction reactions could be dramatically increased by complexation with aromatic solvents and especially with carbon disulfide.[7] Thus, we examined the chlorination reaction in Freon 11 solutions containing large amounts of *tert*-butylbenzene and carbon disulfide, respectively. In the former medium tetrachlorination was indeed inhibited, but the overall yield of dichlorides was

Scheme II



decreased somewhat relative to the yield in pure Freon 11. Attack of chlorine on the hydrogens of the *tert*-butyl group occurred in competition with addition to the Dewar benzene. Chlorination in the presence of carbon disulfide gave slightly less of the tetrachlorides and a slightly higher yield of dichlorides than in Freon 11 alone, and the cis/trans ratio was increased substantially. Unidentified byproducts were formed as well, however, and on balance the solvent of choice remains Freon 11.

Because of the lack of selectivity in chlorination, a longer route that yielded pure *cis*-**5** was developed. We took advantage of the fact that addition of a second equivalent of halogen to either *cis*- or *trans*-**4** occurs exclusively in the exo,cis fashion.[5] The stereoselectivity is a consequence of steric hindrance caused by the halogens that became endo in the first addition; they effectively block attack from the endo face of the remaining double bond (Scheme II).[8]

The mixture of stereoisomeric dibromides **4** was chlorinated in Freon 11. The reaction solution was initially cooled in an ice bath and slowly allowed to come to room temperature. If the mixture was not cooled initially, an extremely vigorous reaction ensued that gave rise to various trichlorobromo and tribromochloro products. A 92% yield of the dibromodichloro compounds **7** was obtained.

Debromination of **7** proceeded smoothly using zinc dust in ether at reflux. *exo,cis*-5,6-Dichlorohexafluorobicyclo[2.2.0]hex-2-ene (*cis*-**5**) was obtained in 81% yield and 98% stereochemical purity. Optimal conditions for the thermal ring opening of **8** were difficult to achieve. After much experimentation it was found that heating the neat olefin at 200 °C for 4 h in sealed, agitated Pyrex ampules containing powdered calcium carbonate as an acid scavenger gave a nearly quantitative yield of *cis*-5,6-dichlorohexafluorocyclohexa-1,3-diene (*cis*-**8**) in >95% purity. The extra precaution of silylating the glass was also observed originally, but this was later found unnecessary. In fact, *excess* silylating agent was found to promote rearrangement of *cis*-**8**, as described below. The infrared spectrum (thin film) of diene *cis*-**8** exhibited double bond stretching bands at 1750 and 1700 cm^{-1}. Its ultraviolet spectrum had λ_{max}(pentane) = 272 nm (ϵ = 2700). The ^{19}F NMR spectrum of *cis*-**8** revealed multiplets at 129.0 (F_5, F_6), 149.7 (F_1, F_4), and 154.5 ppm (F_2, F_3).

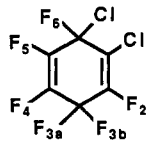
If the thermolysis of *cis*-**5** was carried out in the absence of an acid scavenger, a terrible mixture of products resulted. The major isomer (40%) was isolated by preparative GC and was assigned the structure 1,6-dichloro-

(6) (a) The difference is about 13 kcal/mol. March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley-Interscience: New York; p 23, 624. (b) March, J., ref 6a, p 624.

(7) Russell, G. A. *J. Am. Chem. Soc.* **1958**, *80*, 4997, and earlier papers. See also: Skell, P. S.; Baxter, H. N.; Taylor, C. K. *J. Am. Chem. Soc.* **1983**, *105*, 120–1.

(8) For other examples, see: Barefoot, A. C., III; Saunders, W. D.; Buzby, J. M.; Grayston, M. W.; Lemal, D. M. *J. Org. Chem.* **1980**, *45*, 4292–5.

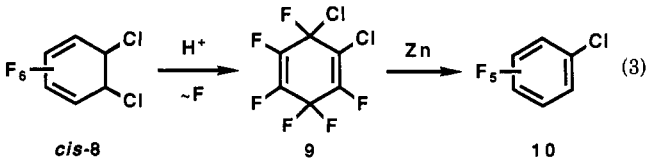
Table I. ^{19}F NMR Analysis of Diene 9



fluorine	δ	coupling constants (Hz)[a]
2	129.5	$J^*_{2,3a} = J^*_{2,3b} = 24$; $J_{2,4} = 1.5$; $J_{2,5} = 3$; $J_{2,6} = 5$
3a, 3b	~109.7[b]	$J^*_{3a,3b}$ = ?; $J^*_{3a,4} = J^*_{3b,4} = 20$; $J^*_{3a,5} = J^*_{3b,5} = 10$; $J^*_{3a,6} = J^*_{3b,6} = 5$
4	159.7	$J_{4,5} = J_{4,6} = 5$
5	143.4	$J_{5,6} = 25$
6	110.8	

[a] J^* is an apparent coupling constant. [b] These fluorines are not isochronous.

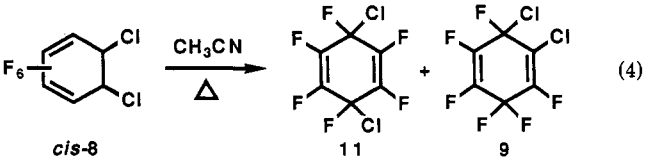
hexafluorocyclohexa-1,4-diene (**9**). Presumably **9** is formed by allylic rearrangement of fluorine in *cis*-**8** (eq 3). The



cis-**8** **9** **10** (3)

infrared spectrum (thin film) of **9** revealed bands at 1770 and 1700 cm^{-1}, and the ultraviolet spectrum had λ_{max}(pentane) = 204 nm (ϵ = 1700). An analysis of the ^{19}F NMR spectrum of **9** is given in Table I. Further proof of structure was provided by zinc reduction of **9** to the known chloropentafluorobenzene (**10**), identified by its ^{19}F NMR spectrum.[9]

A different rearranged product dominated when a dilute acetonitrile solution of diene *cis*-**8** was heated at 180 °C for several hours. In this case a (formal) allylic shift of chlorine occurred to give 3,6-dichlorohexafluorocyclohexa-1,4-diene (**11**). Diene **9** was formed as well, but in much smaller amount (eq 4). The infrared spectrum of



cis-**8** **11** **9** (4)

pure **11** revealed a band at 1742 cm^{-1}. Its ^{19}F NMR spectrum comprised complex symmetrical multiplets at 112.5 (2 F) and 151.6 ppm (4 F), the first resembling a triplet and the second a doublet under low resolution. Zinc reduction of **11** completed the structure proof, giving hexafluorobenzene cleanly.

In the formation of the 1,6-dichloro diene **9**, migration of fluorine in preference to chlorine under conditions of acid catalysis may be understood in terms of the greater bond dissociation energy of the H–F relative to the H–Cl bond (136 versus 103 kcal/mol).[6b] Driving force for the reaction is provided by the *gem*-difluoro effect,[10] and perhaps also by deconjugation of the double bonds (since in the octafluorocyclohexadienes the 1,4- is stabler than the 1,3-isomer).[11]

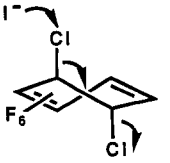
Initially, formation of the 3,6-dichloro diene **11** was thought to occur by an ionization (S_N1) mechanism, but it was found that the rearrangement does not follow first-order kinetics. Apparently the formation of **11** is also a catalyzed process, probably anionotropic. Consistent with the surmise that the reaction is catalyzed, but not by acid, is our observation that presence of the silating agent *N,O*-bis(trimethylsilyl)acetamide in the ring opening of *cis*-**5** increased the amount of **11** formed. In any event, chloride ion should be a much better leaving group than fluoride in acetonitrile solution. The fact that only a single stereoisomer of **11** (of unproven configuration) was formed has interesting mechanistic implications that are the subject of another study.

Pure *trans*-**5** was obtained by preparative gas chromatography from the mixture of cis and trans isomers resulting from direct chlorination of Dewar benzene **3**. Thermolysis under the conditions described above gave *trans*-5,6-dichlorocyclohexadiene (*trans*-**8**) in 98% yield. The IR spectrum (thin film) of this diene showed double bond stretching bands at 1740 and 1700 cm^{-1}; its UV spectrum had λ_{max}(pentane) = 272 nm (ϵ = 3100). Signals at 120.8, 151.0, and 154.6 ppm similar in appearance to those of *cis*-**8** comprised the ^{19}F NMR spectrum.

Not surprisingly, dechlorination of cyclohexadienes **8** to hexafluorobenzene could be effected under very mild conditions, e.g, with sodium iodide in acetone at room temperature. In order to establish the relative reactivity of the cis and trans isomers, mixtures of the two were allowed to compete for iodide ion; the ratio of rate constants was determined by NMR integration using eq 5,

$$k_t = \ln [t]/[t_0] \qquad k_c = \ln [c]/[c_0] \tag{5}$$

where t_0 and c_0 are initial concentrations of the trans and cis isomer and t and c are concentrations during reaction.[12] The ratio k_t/k_c was found to be 16 ± 1 at 25 °C, consistent with the ability of the trans isomer to achieve the favored antiperiplanar geometry in the transition state **12** for E2 elimination. Interestingly, irradiation of *cis*-**8** at 254 nm also transformed it rapidly into hexafluorobenzene.



12

As a preliminary exploration of the Diels–Alder reactivity of dienes **8**, their addition to 4-phenyl-1,2,4-triazoline-3,5-dione was examined. The cis isomer reacted cleanly with this dienophile at 110 °C, yielding a 3:1 mixture of stereoisomeric adducts **13a,b**, respectively. Assignment of **13a** as the major isomer is tentative, based solely on steric considerations. The single adduct **14** derived from *trans*-**8** has only been identified spectroscopically, but competition experiments like those described above have revealed that *trans*-**8** reacts with the triazolidinedione at 110 °C 1.9 ± 0.1 times faster than the cis isomer. Perhaps the rate difference reflects a difference in product stability since the cis adducts, but not the trans, have (formally) eclipsed chlorines.

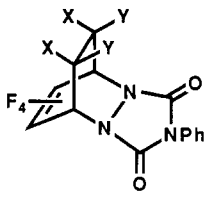
The use of dienes **8** as hexafluorobenzene synthons will be developed in subsequent papers. The choice between

(9) Bruce, M. I. *J. Chem. Soc.* **1968**, 1459–64.

(10) This is the pronounced bond-strengthening effect that accompanies the accumulation of fluorines on the same carbon. Dolbier, W. R., Jr.; Medinger, K. S.; Greenberg, A.; Liebman, J. F. *Tetrahedron* **1982**, *38*, 2415. Dill, J. D.; Schleyer, P. v. R.; Pople, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 1663.

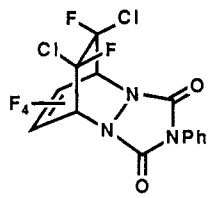
(11) Doyle, A. M.; Patrick, C. R.; Pedlar, A. E. *J. Electroanal. Chem.* **1971**, *33*, 23–30.

(12) Hammett, L. P. *Physical Organic Chemistry*, 2nd ed.; McGraw-Hill: New York, 1970; pp 91–3.



13a X = Cl, Y = F

13b X = F, Y = Cl



14

using pure *cis*-8 or the roughly 1:1 mixture of cis and trans isomers that can be obtained more directly will generally be clear-cut. The availability of a single pure isomer in somewhat better overall yield from perfluorobenzene (63%) than the 1:1 mixture of isomers makes the longer route very attractive. On the other hand, there may be circumstances in which the convenience of the three-step synthesis and/or more facile elimination of trans than cis chlorines at a later stage of a synthetic sequence will justify use of the isomeric mixture.

Experimental Section

Melting points were determined in open capillary tubes and are uncorrected. Solids were analyzed in the infrared as potassium bromide disks, liquids as neat films between sodium chloride disks, and volatiles as gas-phase samples contained in a 10-cm evacuated gas cell equipped with sodium chloride windows. The ^{19}F NMR spectra were obtained at 56.2 MHz on a JEOL FX60Q Fourier transform instrument using fluorotrichloromethane (Freon 11) as an internal standard. Chemical shifts are reported in ppm upfield from the reference. Unless otherwise indicated, deuteriochloroform was used as solvent. Analytical gas chromatograms were obtained with a Hewlett-Packard Model 5880A gas chromatograph using a flame ionization detector and electronic integration. Peak areas were not corrected for differential detector response. Photolyses at 254 nm were conducted in a cylindrical-cavity photoreactor designed by R. Cargill and equipped with 10 25-W GE Type G25T8 lamps and a fan at the base of the cavity. Glass pyrolysis tubes were silylated by adding a few drops of *N,O*-bis(trimethylsilyl)acetamide (Aldrich) and heating the tube over a Bunsen flame in the hood while the liquid made contact with all inner surfaces. The tube was cooled slightly, washed out with two portions of carbon tetrachloride, and dried under vacuum.

All solvents and reagents used in this work were reagent grade unless otherwise noted. Perfluorobenzene was purchased from Fairfield Chemical and zinc dust from Fisher Scientific. The zinc was activated by being stirred with 1 N hydrochloric acid for 5 min, washed with water, and dried under a vacuum; it was stored under argon. Microanalytical data were obtained from Galbraith Labs of Knoxville, TN.

Hexafluorobicyclo[2.2.0]hexa-2,5-diene (3). *Warning: This compound may detonate as a neat liquid.* A large cylindrical quartz vessel (55 × 12 cm) with a 29/42 joint was fitted with a Teflon high-vacuum valve, the joint being well greased with Apiezon H. The vessel was surrounded with a wire screen and evacuated to 0.02 Torr. With the valve closed, the assembly was removed from the vacuum line and the small tube extending from the stopcock was sealed with a rubber septum. To assure rapid and complete evaporation of the reactant into the body of the vessel, the base of the flask was cooled in an ice bath. The valve was reopened and perfluorobenzene (6.0 mL, 9.7 g, 52 mmol) was immediately added via syringe. Now the Teflon valve was resealed and the assembly was clamped into the cylindrical-cavity photoreactor. Fan and lamps were operated for 67 h. The vessel, which now contained no liquid, was carefully removed and clamped inside of a cylindrical wire screen next to a vacuum line. The volatiles were dynamically transferred slowly to a preweighed concentric or U-trap containing 20 mL of Freon 11 and cooled in liquid nitrogen.

Because of the danger of explosion until the Dewar benzene was in solution, the trap contents were allowed to thaw inside of a cylindrical metal screen. The product, 9.2 g (95%), was analyzed by GC (10 ft × $^1/_8$ in. 5% QF-1 on Chromasorb W HP 80/100, 50 °C, 15 mL/min, injection and detection temperature 100 °C) and was found to be 93% hexafluorobicyclo[2.2.0]hexa-2,5-diene and 7% perfluorobenzene. Further purification of the product was not attempted.

5,6-Dibromohexafluorobicyclo[2.2.0]hex-2-ene (4). The bromination of diene **3** was carried out as a modification of a previous procedure.[9] Bromine, 15.9 g (99 mmol), was added dropwise to a stirred ice-cold solution of 19.8 g (96 mmol) of 90% pure diene **3** in 40 mL of Freon 11 while the solution was irradiated with a 75-W sunlamp. The bromine color was discharged almost immediately during addition and its persistence was a good indication of the reaction endpoint. The clear, slightly yellow solution was short-path distilled to remove the solvent and was then distilled under aspirator pressure to yield 32.7 g (98%) of colorless oil, bp 45–50_{17} °C. IR (thin film): 1765, 1370, 1125, 970, 850, 820, 745 cm^{-1}. ^{19}F NMR ($CDCl_3$): exo,cis 113.7, 116.5, 174.3 ppm; trans 101.8, 108.0, 115.8, 117.9, 171.5, 191.5 ppm. ^{19}F NMR as well as GC analysis (25-m methylsilicone capillary column, 50 °C, 18 psi) revealed a 7 to 3 ratio for the exo,cis (t_R = 4.60 min) to trans (t_R = 4.35 min) isomers.

Thermolysis of 5,6-Dibromohexafluorobicyclo[2.2.0]hex-2-ene (4). (a) Neat at 160–180 °C. A small, heavy-walled, freshly silylated Pyrex ampule was filled with 0.1 g of a mixture of **4** isomers and sealed under vacuum. The tube was heated for 30 min at 160 °C. After cooling, it was cracked open and GC analysis (25-m methylsilicone capillary column, 50 °C, 18 psi, 175 °C, injection and detection temperature) of the clear red solution revealed perfluorobenzene (6%), *trans*-**4** (27%), *cis*-**4** (66%), and two peaks of longer retention time (0.5%). Thermolysis at 180 °C for 20 min gave 54% perfluorobenzene, 8% *trans*-**4**, 48% *cis*-**4**, and no other products.

(b) Flow Pyrolysis at 220 °C. A small amount of **4** was pyrolyzed in a 30 × 0.8 cm glass-helix-packed Pyrex hot tube attached to a cold trap. The tube was heated to 220 °C and evacuated to 14 Torr; the trap was cooled with use of a dry ice/2-propanol bath. Dibromo compounds **4** passed through the tube at 20 mg per min, and after 5 min the trap was removed and warmed. Its red liquid content was diluted with Freon 11 and analyzed by GC (25-m methylsilicone capillary column, 50 °C, 18 psi, 175 °C injection and detection temperature), revealing perfluorobenzene (54%), *trans*-**4** (9%), *cis*-**4** (36%), and four other compounds of longer retention time (~1% total). Pyrolysis at 300 °C gave only perfluorobenzene.

***exo,cis*- and *trans*-5,6-Dichlorohexafluorobicyclo[2.2.0]-hex-2-ene (5).** The chlorination of diene **3** was carried out as a modification of a previous procedure.[9] A solution of 29.0 g of 90% pure diene **3** (0.156 mol) in 120 mL of Freon 11 was poured into a tightly clamped 88-mL heavy-walled Fischer-Porter tube wrapped with aluminum foil and was cooled in an ice bath. The tube was connected via a valve and a flexible spiral of copper tubing to a lecture bottle of chlorine mounted on a top-loading balance. Chlorine, 12.7 g (0.179 mol), was added over the course of 5 min to the vigorously stirred solution, with flow controlled at the reactor end of the spiral to assure accurate weighing. Stirring was continued as the ice melted; then the yellow solution was stirred at room temperature overnight. GC analysis (25-m dimethylsilicone capillary column 40 °C, 18 psi) revealed 15% unreacted **3**, 15% perfluorobenzene, 50% of the dichloro compounds **5**, and 20% tetrachloro adducts **6**. After the solvent and unreacted starting material were removed by distillation through a 20-cm Vigreux column, the product was distilled to yield 21.6 g (55%) of 85% pure dichloro adducts **5** (cis/trans 1:1), bp 95–103 °C. The pot contained 16.1 g (31%) of almost pure tetrachloro adducts **17**.

A sample of the mixture of stereoisomeric dichlorides was separated by preparative GC. ^{19}F NMR ($CDCl_3$): exo,cis 115.3, 116.6, 182.0; trans 108.3, 115.9, 117.0, 117.7, 180.7, 192.7 ppm. IR (neat): exo,cis 1760, 1370, 1130, 860, 760; trans 1750, 1350, 1130, 860, 720 cm^{-1}. MS (both) *m/e*: 256 (M^+), 221 ($C_6F_6Cl^+$, base), 186 ($C_6F_6^+$), 171 ($C_5F_4Cl^+$).

2,3-Dibromo-5,6-dichlorohexafluorobicyclo[2.2.0]hexane (7). The chlorination was carried out as described for **3**. Chlorine, 9.2 g (130 mmol), was added to an ice-cooled, stirred solution of 42.0 g (121 mmol) of dibromo compounds **4** in 25 mL of $CFCl_3$. The ice bath was allowed to melt slowly and the solution was

stirred at room temperature for 24 h. After distillation of the solvent, the product was distilled under aspirator pressure (bp $90–95_{20}$ °C) to give 47.0 g (93%) of oil. ^{19}F NMR: cis dichloro, cis dibromo 119.0, 120.0, 151.3; cis dichloro, trans dibromo 99.7, 110.8, 118.5, 120.5, 151.7, 170.3 ppm. IR (thin film): 1295, 1205, 1170, 1035, 805, 770, 720 cm^{-1}. Gas chromatographic analysis (25 m dimethylsilicone capillary column 50 °C for 3 min, then 15°/min to 150 °C, 18 psi, 175 °C injection and detection temperature) revealed a ratio of 7 to 3 for the cis dichloro, trans dibromo (t_R = 9.5 min) to cis dichloro, cis dibromo (t_R = 9.1 min) compounds. Anal. Calcd: C, 17.28; F, 27.36; Br, 38.34. Found: C, 17.57; F, 27.14; Br, 38.16.

***cis*-5,6-Dichlorohexafluorobicyclo[2.2.0]hex-2-ene (*cis*-5).** In a 500-mL three-necked flask was placed 13.7 g (0.21 mol) of activated zinc dust (Fisher) in 100 mL of anhydrous ether. Roughly 12 mL of a solution of 82.0 g (0.197 mol) of the dibromodichloro compound **7** in 70 mL of anhydrous ether was added from a dropping funnel, with a good condenser bearing a drying tube in another neck of the flask. The mixture was vigorously stirred and warmed until the exothermic reaction began. Then the balance of the material was added at such a rate as to maintain reflux. After the addition heating was begun again and the mixture was refluxed another 3.5 h. The mixture was cooled, washed with water (2 × 100 mL) and saturated brine (100 mL), dried over sodium sulfate, and filtered. Ether was removed through a 10-in. helix-packed, vacuum-jacketed and silvered distillation column. The product was then distilled at atmospheric pressure through a short Vigreux column, the bulk of the material distilling at 104–105 °C. This colorless, mobile liquid (41.2 g, 0.160 mol) was obtained in 81% yield and in excellent purity as judged by ^{19}F NMR ($CDCl_3$), which showed signals at 115.3, 116.6, 182.0 ppm. IR (thin film): 1760, 1370, 1130, 860, 760 cm^{-1}. GC (25-m dimethylsilicone capillary column, 50 °C, 14 psi, 175 °C injection and detection temperature): t_R 4.3 min.

Attempted Reaction between *cis*-5 and Hexafluoropropylene Oxide. A stainless steel bomb fitted with a bellows-seal valve was filled with 2.0 g (7.8 mmol) of *cis*-**5** and 1.3 g (7.8 mmol) of hexafluoropropylene oxide. The bomb was heated at 185 °C for 1 $^1/_2$ h. After it had cooled to room temperature, the valve was cracked open and gaseous products were allowed to escape up the hood. The remaining volatiles were dynamically transferred to a U-bulb. Analysis by ^{19}F NMR spectroscopy revealed almost no reaction and no new signals consistent with a cyclopropane adduct, as judged by the lack of any new high field signals.

***cis*-5,6-Dichlorohexafluorocyclohexa-1,3-diene (*cis*-8).** A clean, heavy-walled 10-mL Pyrex bomb was filled with 0.25 g of calcium carbonate and 7.0 g (27.3 mmol) of of *cis*-**5**. The tube was attached to a vacuum line, put through 2 freeze–pump–thaw cycles, frozen, and sealed under vacuum. The glass tube was mounted in a metal pipe, which was wrapped with heating tape and clamped horizontally to a Kugelrohr rocker. Temperature was monitored by using a thermocouple attached to the glass tube with asbestos tape and was controlled by using an Omega Model 149 temperature controller. The tube was heated at 200 °C with gentle rocking for 4 h. After cooling, it was cracked open and the clear liquid, 6.0 g, was dynamically vacuum transferred to a U-bulb. GC analysis (25-m methylsilicone capillary column, 14 psi, 40 °C) revealed 2% starting material, 2% rearranged products, and 96% pure diene **13**. UV: λ_{max} (pentane) 272 nm (ϵ = 2700, corrected for impurities). ^{19}F NMR ($CDCl_3$): 129.0 (F_5, F_6), 149.6 (F_1, F_4), 154.0 ppm (F_2, F_3). IR (thin film): 1750, 1700, 1405, 1345, 1235, 1015, 990, 880, 850 cm^{-1}. MS (70 eV) *m/e*: 256 (M^+), 221 ($C_6F_6Cl^+$), 202 ($C_6F_5Cl^+$), 186 ($C_6F_6^+$, base), 171 ($C_5F_4Cl^+$), 117 ($C_5F_3^+$). At 35 eV, *m/e* 221 became the base peak. Anal. Calcd: C, 28.02; F, 44.39. Found: C, 27.82; F, 44.23.

Reduction of *cis*-8. (a) By Iodide Ion. To a 5-mm NMR tube at room temperature were added 0.12 g of *cis*-**8** (0.5 mmol) and 0.5 mL of acetone-d_6. Sodium iodide, 0.020 g (0.1 mmol), was added and upon shaking the solution turned orange-brown immediately. An NMR spectrum revealed starting material (~80%) and perfluorobenzene (20%). Additional sodium iodide, 0.020 g (0.1 mmol), caused a similar increase in perfluorobenzene content.

(b) By UV Irradiation. A 5-mm quartz NMR tube was filled with a solution of 4 mg of *cis*-**8** in 1 mL of spectrometric grade pentane. The tube was irradiated at 254 nm at room temperature for 4 min. An ^{19}F NMR spectrum revealed about 80% reaction of the diene to give perfluorobenzene as the sole organic product.

***trans*-5,6-Dichlorohexafluorocyclohexa-1,3-diene (*trans*-8).** A sample of *trans*-**5** was ring-opened to the diene in 98% yield by the method described for the cis isomer. UV: λ_{max} (pentane) 272 nm (ϵ = 3100). ^{19}F NMR ($CDCl_3$): 120.8 (F_5, F_6), 151.0 (F_1, F_4), 154.6 ppm (F_2, F_3). IR (neat): 1740, 1700, 1400, 1340 cm^{-1}. The mass spectrum resembled that of the cis isomer very closely, but *m/e* 186 was the base peak at 35 eV as well as 70 eV. Anal. Calcd: C, 28.02; Cl, 27.63. Found: C, 28.30; Cl, 27.78.

1,6-Dichlorohexafluorocyclohexa-1,4-diene (9). The title compound **9** was formed on numerous occasions during the thermolysis of *cis*-**5** when an acid scavenger was not present. On one occasion it was the major component (40%) along with many other rearranged products. A pure sample of **9** was isolated by preparative GC (10 ft × $^1/_4$ in. 10% SF-96 on Chromasorb W HP 80/100, 60 °C, 160 mL/min). IR (thin film): 1770, 1700, 1320, 1198 cm^{-1}. ^{19}F NMR ($CDCl_3$): 109.7, 110.8, 129.5, 143.4, 159.7 ppm (see Table I). UV: λ_{max} (pentane) 204 nm (ϵ = 1700). Anal. Calcd: C, 28.12; F, 44.53. Found: C, 27.86; F, 44.27.

A mixture of **9** (60%), *cis*-**8** (20%), perfluorobenzene (15%), and several minor components, 0.10 g, in 1 mL of glacial acetic acid was stirred at room temperature. Zinc dust, 0.1 g, was added in one portion. The mixture warmed but cooled to ambient temperature after 10 min. The excess zinc was allowed to settle and the clear solution was removed. This was added to 1 mL of deuteriochloroform, washed with water, and dried (Na_2SO_4). An ^{19}F NMR spectrum revealed perfluorobenzene and chloropentafluorobenzene (**10**), 141.3 (2 F), 161.9 (2 F), 156.7 ppm (1 F). The chemical shifts match literature values.[9]

3,6-Dichlorohexafluorocyclohexa-1,4-diene (11). A solution of 0.25 g (1.0 mmol) of *cis*-**8** in 5 mL of freshly distilled (CaH_2) acetonitrile was poured into a 10-mL heavy-walled Pyrex bomb. The bomb was frozen and sealed under vacuum. After heating in an oil bath maintained at 170 °C for 5 h, the bomb was cooled and cracked open. GC analysis (25-m dimethylsilicone capillary column, 40 °C, 14 psi) revealed starting *cis*-**8** (20%), rearranged diene **9** (10%), and the sought-after rearranged diene **11** (70%). The dark solution was vacuum transferred to give a clear, colorless solution. Concentration of the fluorocarbon products by large-scale preparative GC (400 μL per injection, 10 ft × $^1/_4$ in., 15% Carbowax 20 M on Chromasorb W HP, 90 °C, 160 mL/min) followed by preparative GC of this mixture (10 ft × $^1/_4$ in. 10% SF-96 on Chromasorb W HP, 60 °C, 160 mL/min) gave 70 mg of 97% pure **11**. ^{19}F NMR ($CDCl_3$): 112.5 ppm (F_3, F_6), 151.6 ppm (F_1, F_2, F_4, F_5). IR (gas phase): 1742, 1540, 1320, 1195, 1050, 990 cm^{-1}. Anal. Calcd: C, 28.12; F, 44.53. Found: C, 28.26; F, 43.89.

A solution of ~10 mg of diene **11** in 0.4 mL of dry glyme was treated with an excess of zinc dust and was warmed to 40 °C for 10 min. The clear colorless solution was removed from the remaining zinc dust. ^{19}F NMR analysis revealed complete conversion to perfluorobenzene.

Diels–Alder Reaction of 8 with 4-Phenyl-1,2,4-triazoline-3,5-dione. A solution of 0.38 g (1.5 mmol) of *cis*-**8** and 0.25 g (1.4 mmol) of freshly sublimed ($100_{0.05}$ °C) 4-phenyl-1,2,4-triazoline-3,5-dione in 6 mL of methylene chloride was poured into a 10-mL heavy-walled glass bomb and sealed under vacuum. The tube was heated in a pipe wrapped with heating tape at 110 °C for 23 h. After cooling, the clear brown solution was evaporated at room temperature. ^{19}F NMR revealed almost complete disappearance of starting *cis*-**8** and two new compounds, **13a,b**, in a ratio of 3 to 1, respectively. Signals for the major one appeared at 127.3, 144.5, 174.7 ppm and for the minor one at 122.2, 143.0, 175.4 ppm. The semicrystalline brown mass was sublimed at $120_{0.03}$ °C) to give a white solid, mp 115–122 °C. Recrystallization from ether (–28 °C) gave beautiful long white needles of the major isomer (**13a**), 0.08 g (13%), mp 132.5–134 °C. MS: *m/e* 431 (M^+), 396 (M^+ – Cl), 299, 221, 186, 119 (base, $PhNCO^+$). ^{19}F NMR ($CDCl_3$): 127.3 (F's gem to Cl), 144.5 (vinyl F's), 174.7 ppm (bridgehead F's). IR (KBr): 3090, 1811, 1782, 1755, 1745, 1595, 1405, 980, 830 cm^{-1}. Anal. Calcd: C, 38.90; H, 1.16; F, 26.40. Found: C, 39.09; H, 1.35; F, 26.12.

When a mixture of *cis*- and *trans*-8 was allowed to react at 110 °C with the triazolinedione, NMR signals for the trans adduct 14 appeared together with those for the two cis compounds (13a,b). ^{19}F NMR ($CDCl_3$) for 14: 104.5 (F gem to Cl, distal to N), 113.5 (F gem to Cl, proximal to N), ~144 (vinyl F's, overlap with 13a,b signals), ~176 ppm (bridgehead F's, overlap with 13b signal).

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

1,2-Cycloadditions to *cis*-5,6-Dichlorohexafluorocyclohexa-1,3-diene[1]

William P. Dailey, Philip Ralli, David Wasserman, and David M. Lemal*

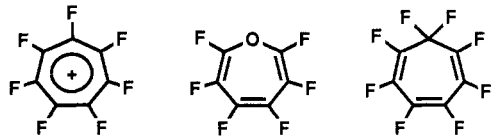
Department of Chemistry, Dartmouth College, Hanover, New Hampshire 03755

Received October 4, 1988

Addition of difluorocarbene to the title compound (7) at temperatures of 160–190 °C yielded rearranged monoadducts having the norbornene and bicyclo[3.2.0]hept-2-ene skeletons. Dechlorination of these compounds gave octafluoronorbornadiene (21) and octafluorobicyclo[3.2.0]hepta-2,6-diene (22). Though attempts to transform 22 into tropylium ion 1 met with failure, norbornadiene 21 was so transformed, as elaborated elsewhere. Addition of chlorofluorocarbene to 7 at 130 °C gave a stereoisomeric mixture of cyclopropanes (1:1 adducts), which were stable under the reaction conditions. Treatment of 7 with peroxytrifluoroacetic acid yielded a single monoepoxide (36). Reduction of 36 under mild conditions gave not the expected benzene oxide 2 but pentafluorophenol.

Introduction

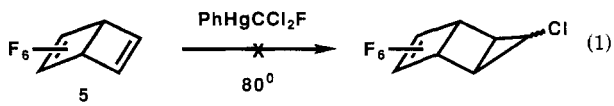
The work described in this paper was stimulated by a desire to synthesize the heptafluorotropylium ion (1) and hexafluorooxepin (2). An appropriate precursor for 1,



1 2 3

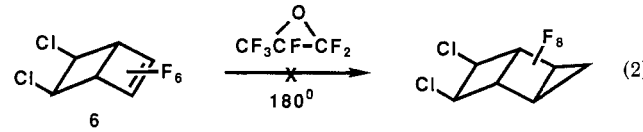
octafluorocycloheptatriene (3), had been synthesized previously by Tatlow's group,[2] but by a very long and low-yield route. A more practical method was needed, and the relatively inexpensive hexafluorobenzene (4) was an appealing starting material.

Direct addition of difluorocarbene to hexafluorobenzene requires violent conditions and yields only insertion products, octafluorotoluene and others.[3] Thus a hexafluorobenzene synthon, far more reactive than the compound itself, was required. At the outset, we envisioned carbene addition to the synthon hexafluoro Dewar benzene (5), which is available in excellent yield from the benzene by vapor-phase irradiation.[4] The resulting adduct was to be ring opened thermally to give the desired cycloheptatriene skeleton. Unfortunately, attempts to add chlorofluorocarbene to 5 at temperatures below 80 °C, where ring opening to 4 becomes fairly rapid, met with failure (eq 1). Halogenation of one of the double bonds of 5 results in greatly increased thermal stability,[5] thus



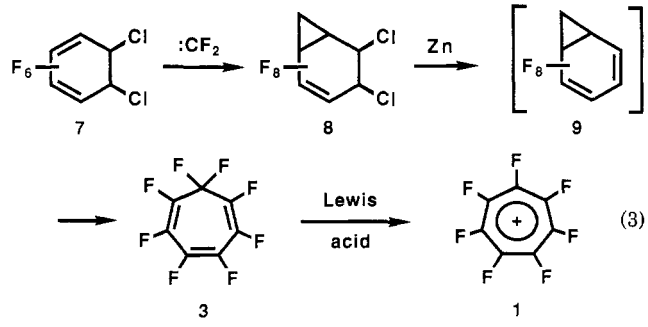
5 (1)

extending the temperature range available for carbene addition. It was found, however, that 5,6-dichlorobicyclo[2.2.0]hex-2-ene 6 resists addition of difluorocarbene (generated by pyrolysis of hexafluoropropylene oxide) even at temperatures around 180 °C (eq. 2).



6 (2)

We discovered that Dewar benzene 5 was also inert to peroxytrifluoroacetic acid at room temperature, but that a perfluorinated cyclohexa-1,3-diene underwent epoxidation under these conditions. These observations suggested that the cyclohexadiene 7 formed by thermal ring opening of bicyclohexene 6 might be capable of cyclopropanation with fluorinated carbenes. If so, 7 might serve as a hexafluorobenzene synthon en route to the heptafluorotropylium ion (1). Reductive dechlorination of the adduct 8 would yield via octafluoronorcaradiene (9) the triene 3,[6] which should be easily transformed by a Lewis acid into the ion 1 (eq 3).



7 8 9 3 1 (3)

As described in a previous paper,[7] we have developed a synthesis of 7 from the benzene 4 in 63% overall yield. Here we present the results of cyclopropanation and epoxidation experiments on this compound.

(1) This paper is based principally on the Ph.D. Dissertation of W. P.D., Dartmouth College, 1983.

(2) Dodsworth, D. J.; Jenkins, C. M.; Stephens, R.; Tatlow, J. C. *J. Chem. Soc. Chem. Commun.* **1972**, 803–4.

(3) Vorozhtsov, N. N.; Ermolenko, N. V.; Mazalov, S. A.; Osina, O. M.; Platonov, V. E.; Tyurin, V. S.; Yakobson, G. C. *J. Gen. Chem. USSR (Engl. Trans.)* **1969**, 195.

(4) Camaggi, G.; Gozzo, F.; Cevidalli, G. *J. Chem. Soc. Chem. Commun.* **1966**, 313–4. Haller, I. *J. Am. Chem. Soc.* **1966**, *88*, 2070–1.

(5) Harrison, E., III, Senior Thesis, Dartmouth College, 1981. Lawlor, D., unpublished results.

(6) For the parent norbornadiene and its relationship to cycloheptatriene, see: Rubin, M. *J. Am. Chem. Soc.* **1981**, *103*, 7791–2.

(7) Dailey, W. P.; Correa, R. A.; Harrison, E., III; Lemal, D. M. *J. Org. Chem.*, previous paper in this issue.

0022-3263/89/1954-5516$01.50/0