triple ions formed between the heteroatoms and the cations differ in detail due to the mode of puckering, and it is these modes of puckering that cause the manifold of topologically different structures in these systems and that ultimately determine the relative energies of the resulting structures. Different triple ion structures differ little in energy and are readily interconverted.

The calculated structures are those for gas-phase monomers; the true species in solution are undoubtedly both solvated and aggregated. Nevertheless, the same fundamental principles identified for the monomeric triple ions probably apply to the aggregates as well; in particular, the observed syn regiochemistry is found for the monomers and does not require any unusual cooperative effects within dimers or higher aggregates. The regioselective syn deprotonation and the regioselective addition of an electrophile to the syn α-carbon appear to be direct consequences of the pronounced trend for the preferential formation of triple ions centered at the heteroatoms.

Acknowledgment. This research was supported in part by NSF grants. We thank the San Diego Supercomputer Center and the Campus Computer Facility, UCB, for generous grants of computer time on Cray II and VAX 8800 computers, respectively.

Supplementary Material Available: Structures (in **Z**-matrix form), total and relative energies, and vibrational frequencies of structures **1**–**13** given in Appendix I and structures (in **Z**-matrix form) and heats of formation of structures M1–M8 given in Appendix II (MNDO and AM1) (15 pages). Ordering information is given on any current masthead page.

Synthesis and Chemistry of Highly Fluorinated Bicyclo[2.2.0]hexenones[1]

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A series of highly fluorinated bicyclo[2.2.0]-5-hexen-2-ones (**3**) and their hydrates (**4**) have been prepared in two steps from hexafluoro Dewar benzene (**1**). Photolysis of *exo*-3*H*-pentafluorobicyclo[2.2.0]-5-hexen-2-one (**3d**) at low pressure in the vapor phase gave 1*H*-pentafluorocyclopentadiene (**8**), but in solution the principal product was pentafluorophenol (**9**). Under Favorskii conditions, *exo*-3-bromo- and *exo*-3-chloropentafluorobicyclo[2.2.0]-5-hexen-2-one (**3a** and **3b**) ring opened stereospecifically to 2-cyclobutenecarboxylic acids **17** and **29**, respectively. Treatment of these ketones with *tert*-butoxide under aprotic conditions effected stereospecific cleavage to *tert*-butyl methylenecyclobutenecarboxylates **25** and **30**. The acid (**27**) corresponding to **25** was obtained both from bromohydrate **4a** and the acid **17**, again stereospecifically, by reaction with lithium diisopropylamide. Flash vacuum pyrolysis of the hydrate (**4c**) of hexafluorobicyclo[2.2.0]-5-hexen-2-one at 300 °C gave hexafluoro-2,4-cyclohexadienone (**12**), which decarbonylated at higher temperatures to yield hexafluorocyclopentadiene (**13**). Similarly, flash vacuum pyrolysis of 3-chloropentafluorobicyclo[2.2.0]-5-hexen-2-one (**3b**) at 650 °C gave a mixture of 1- and 2-chloropentafluorocyclopentadienes.

Pentafluorocyclopentadienes bearing hydrogen or halogen at the 5-position are potential sources of the pentafluorocyclopentadienyl ligand, a ligand which holds promise of becoming quite important in organotransition metal chemistry.[2] Prior to our studies, syntheses of pentafluorocyclopentadienes[3] and the perfluoro compound[4] were based on fluorination of appropriate five-membered ring precursors. Typically, they involved complicated product mixtures and low yields. We were thus led to consider quite different routes to this family of compounds.[5] In particular, we were attracted to hexafluorobenzene as a starting material because it is readily available, relatively inexpensive (for a fluorocarbon), and capable of being photoisomerized easily in excellent yield to the reactive hexafluoro Dewar benzene (**1**).[7,8] As will become clear, our schemes for ring contracting this compound to produce bicyclo[2.1.0]pentenes and their cyclopentadiene valence isomers have gone awry, for the most part. Nonetheless, they have led to unusual chemistry, to examples of remarkable stereoelectronic control, and to a family of highly

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(1) This paper is based principally on the Ph.D Dissertation of R. R. Soelch, Dartmouth College, 1984.

(2) High promise is suggested by (1) the ubiquity of the cyclopentadienyl ligand in organotransition metal chemistry, (2) the striking changes in reactivity of its complexes which substitution on that ligand can produce (cf. pentamethylcyclopentadienylmetal chemistry), and (3) the fact that other perfluorinated ligands form a wealth of stable complexes with transition metals.

(3) (a) Banks, R. E.; Bridge, M.; Haszeldine, R. N.; Roberts, D. W.; Tucker, N. I. *J. Chem. Soc. C* **1970**, 2531–2535. (b) Fields, R.; Green, M.; Harrison, T.; Haszeldine, R. N.; Jones, A.; Lever, A. B. P. *J. Chem. Soc. A* **1970**, 49–58. Bergomi, A.; Burdon, J.; Tatlow, J. C. *Tetrahedron* **1966**, 2551–2554.

(4) Banks, R. E.; Bridge, M.; Haszeldine, R. N. *J. Chem. Soc. C* **1970**, 48–49 and references therein. Moore, E. P., U.S. Patent No. 3,686,336, 1972; *Chem. Abstr.* **1973**, *78*, P3832*u*. Harris, J. F., Jr.; U.S. Patent No. 3,449,304, 1969. Burdon, J.; Hodgins, T. M.; Perry, D. R. A.; Stephens, R.; Tatlow, J. C. *J. Chem. Soc.* **1965**, 808–810.

(5) In addition to the routes described in this paper, we have developed other pathways to some of these highly fluorinated cyclopentadienes.[6]

(6) (a) Soelch, R. R.; Mauer, G. W.; Lemal, D. M. *J. Org. Chem.* **1985**, *50*, 5845–5852. (b) Unpublished work by these authors.

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

(8) Sixty percent conversion of the benzene to its Dewar isomer has been reported, but we have found that longer irradiation times increase the conversion (and yield) to about 90%.

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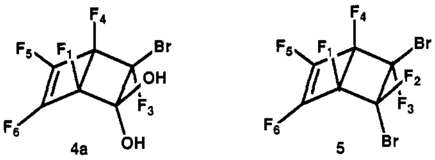
Table I. ^{19}F NMR and IR Data for Bicyclo[2.2.0]hexene Derivatives

compd	NMR solvent[a]	chemical shifts[b] vinyl (F_5, F_6)	F_3	bridgehead (F_1, F_4)	IR (cm^{-1})[c] C=O, C=C
1	THF	121.4 (4 F)		188.5 (2 F)	1750
2	acetonitrile	120.3, 123.3	126.7	182.8, 188.4	1750, 1710
3a	THF	114.2, 115.0	119.9	181.8 (2F)	1850, 1755
3b	acetonitrile	112.3 (3 F)		180.6, 187.7	1850, 1750
3d	acetonitrile	112.9, 119.3	186.4[d]	181.5, 183.2	1850, 1750
4a	THF	115.0, 119.9	114.2	177.8, 194.4	1755
4b	acetonitrile	115.5, 116.9	121.5	184.4, 193.4	1755
4c	acetonitrile	115, 117	126.4[e]	196 (2F)	1755
4d	acetonitrile	120.7, 121.8	192.6	180.9, 195.3	1750

[a] Acetonitrile was deuterated in all cases except 3d, where a 1:1 mixture with ordinary acetonitrile was used. [b] Given in ppm upfield from trichlorofluoromethane; *individual* assignment of vinyl and bridgehead fluorines is not implied. [c] Conditions for the IR measurements are given in the Experimental Section. [d] J_{HF} = 50.5 Hz. [e] AB quartet, J_{gem} = 202 Hz.



Chemical Shifts

	F_1	F_2	F_3	F_4	F_5	F_6
4a	194.4	---	114.1	177.8	118.5	123.1
5	195.8	109.6	103.2	175.0	119.4	121.0

Coupling Constants (Hz)

J	4a	5
1,2	---	10.2
1,3	5.8	4.0
1,4	2.9	1.4
1,5	3.8	7.4
1,6	17.5	19.0
2,3	---	11.0
2,4	---	3.0
2,5	---	5.6
2,6	---	1.8

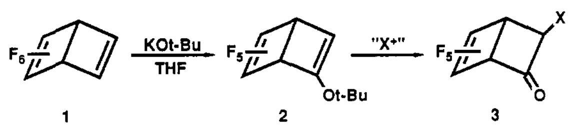
J	4a	5
3,4	5.8	5.6
3,5	0.5	2.0
3,6	1.8	1.0
4,5	16.6	17.0
4,6	7.0	5.6
5,6	11.5	12.0

Figure 1. ^{19}F NMR data for hydrate **4a** and model compound **5**. Fluorines in **5** have been numbered unconventionally for easy comparison with those of **4a**.

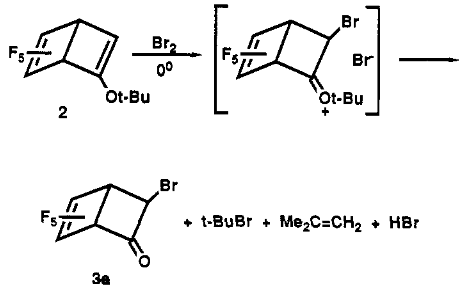
reactive compounds which may serve as synthetic intermediates en route to other interesting fluorocarbon derivatives.

Results and Discussion

Fluorinated Bicyclo[2.2.0]-5-hexen-2-ones (3) and Their Hydrates (4). Of central importance in our plans were 3-substituted pentafluorobicyclo[2.2.0]-5-hexen-2-ones (**3**). We envisioned preparing them by attack of appropriate electrophiles on *tert*-butyl enol ether **2**, which we were able to obtain in 50–60% yields by the reaction of potassium *tert*-butoxide with Dewar benzene **1** in tetrahydrofuran at −23 °C.[9] Hexafluoro Dewar benzene is a dangerous compound which detonates capriciously as a neat liquid.[10,11] For this reason we handle it exclusively in solution after its creation in the gas phase. In contrast, the derived *tert*-butyl ether **2** has been handled in pure form for years without incident. Double bond stretching bands in the infrared spectrum of **2** at 1750 and 1710 cm^{-1} reveal the presence of the FC=CF and FC=CO moieties, respectively.[12] These values and the ^{19}F NMR spectral data presented in Table I constitute strong evidence for the structure of this *tert*-butyl ether. It is noteworthy that vinyl and bridgehead fluorines differ in chemical shift by 60–70 ppm in **1**, **2**, and throughout the family of compounds to be discussed which we have derived from **2** (Table I).

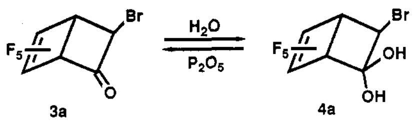


Bromine reacted instantly with **2** at 0 °C, yielding *exo*-3-bromopentafluorobicyclo[2.2.0]-5-hexen-2-one (**3a**), *tert*-butyl bromide, isobutylene, and hydrogen bromide.



The last three components were identified by IR analysis, and the *tert*-butyl bromide by GC as well. Typically, the ratio of *tert*-butyl bromide to ketone was about 0.4. Only a single stereoisomer of the bicyclohexenone was formed; its configuration was assigned as exo on the basis of analogy and confirmed by the NMR analysis described below. The analogies were provided by Camaggi and Gozzo[10] and by Haszeldine's group,[11] who showed that addition reactions to diene **1** exhibit a marked preference for exo attack, presumably for steric reasons. In particular, bromine adds to form a mixture of trans (**5**) and exo, cis dibromide: the endo, cis isomer is absent.

The carbonyl group in **3a** was revealed by a stretching band in the infrared spectrum at 1850 cm^{-1}, a very high frequency because of ring strain and fluorine substitution in its vicinity. The same combination of circumstances causes the carbonyl group to hydrate voraciously, transforming a mobile, volatile liquid ketone into a nonvolatile, crystalline *gem*-dihydroxy compound (**4a**).[13] If the glassware and reagents used to prepare **3a** are not thor-



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[9] The Dewar benzene had previously been treated with ethoxide ion to give a mixture of diethers[10] and with methoxide ion to give (depending upon the stoichiometry) either a monoether analogous to 2 or a diether mixture.[11]

[10] Camaggi, G.; Gozzo, F. *J. Chem. Soc. C* **1969**, 489–500.

[11] Barlow, M. G.; Haszeldine, R. N.; Morton, W. D.; Woodward, D. R. *J. Chem. Soc., Perkin Trans. 1* **1972**, 2170–2180.

[12] Corresponding values for the methyl ether are 1763 and 1734 cm^{-1}, respectively.[11] Better agreement for the O-substituted double bond of 2 is found with the 2,5- and 2,6-diethoxy derivatives of 1, which display a band at 1715 cm^{-1}.[10]

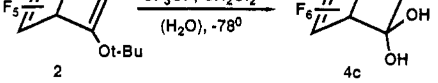
[13] Hexafluorocyclobutanone, for example, forms a very stable hydrate.[14]

[14] England, D. C. *J. Am. Chem. Soc.* **1961**, *83*, 2205.

oughly dry, in fact, a significant amount of hydrate accompanies ketone in the product. Treatment of the hydrate with phosphorus pentoxide regenerates the ketone in quantitative yield. This fact, together with the dramatic differences in physical properties between **3a** and **4a**, make hydration a useful procedure for purifying the ketone. Trap-to-trap distillation of the reaction mixture from bromination of **2** easily separates the ketone from everything but *tert*-butyl bromide, which is very similar in volatility to **3a**. Addition of 1 equiv of water causes the hydrate to crystallize; the *tert*-butyl bromide is then pumped off, leaving behind analytically pure hydrate in 70% overall yield. Though the ketone can be regenerated at this stage, it is convenient to store it as the hydrate. Whereas the former decomposes over several days at room temperature in vacuo and in the dark, the latter shows no sign of deterioration after storage at room temperature for many months.

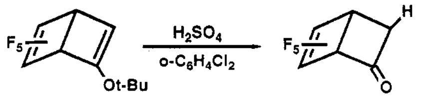
Reaction of **2** with chlorine gave *exo*-3-chloropentafluorobicyclo[2.2.0]-5-hexen-2-one (**4b**) in 70% yield, again with no significant contamination by the endo isomer. In this case the ketone was obtained pure simply by distillation from the reaction mixture since it was much less volatile than the byproduct *tert*-butyl chloride.

In a first attempt to prepare hexafluorobicyclo[2.2.0]-5-hexen-2-one (**3c**), enol ether **2** was treated with perchloryl fluoride[15] at temperatures up to 45 °C, but no reaction occurred. When trifluoromethyl hypofluorite[16] was bubbled into a methylene chloride solution of **2** at room temperature under nitrogen, a yellow flash was observed followed by an explosion. Apparently isobutylene formed in the desired reaction had formed an explosive mixture with the fluorinating agent in the head space of the reaction vessel. Repetition of the reaction at −78 °C in a special reactor which allowed for flushing of the head space with nitrogen gave ketone **3c** as its hydrate **4c** (because of the presence of adventitious water) in 71% yield. Unlike hydrates **4a** and **4b**, this compound was found to be quite labile even after numerous sublimations and recrystallizations. The geminal fluorines gave rise to an AB quartet in the ^{19}F NMR spectrum, J = 202 Hz.



2 4c

Addition of concentrated sulfuric acid to a solution of enol ether **2** in *o*-dichlorobenzene produced the exo-3*H* ketone **3d** in 85% yield. The fluorine at C_3 which had been responsible for the signal at 126.7 ppm in **2** now appeared at 185.9 ppm, and the assignment was confirmed by the 50-Hz splitting of this resonance by the geminal hydrogen.

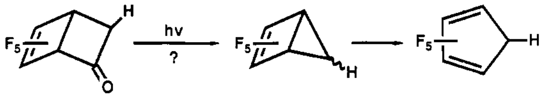


2 3d

^{19}F NMR data for the series of ketones and their hydrates are summarized in Table I, together with key IR bands. We present here a complete analysis of the ^{19}F NMR spectrum of one member of the set, bromohydrate **4a**, both as a representative example and as confirmation of the exo configurational assignment. The coupling constants for the bromohydrate were obtained with the help of computer simulation. Its resonances were assigned principally by comparison of its coupling constants and chemical shifts[17] with the known values for *trans*-5,6-dibromohexafluorobicyclo[2.2.0]-2-hexene (**5**) (Figure 1).[18]

The distinction between the high-field bridgehead fluorines and the others is immediately obvious; the vinyl fluorines are revealed not only by the similarity of their chemical shifts to those of **5**, but more convincingly by their strong coupling to the adjacent bridgehead fluorines and to one another. Therefore, the remaining, much narrower, resonance is attributable to F_3, whose coupling constants to the other four fluorines deviated by an average of only 1.1 Hz from those of F_3 in **5**. The substantial disparity (11 ppm) in chemical shift between the F_3's in **4a** and **5** is easily accounted for by the deshielding effect of the cis, vicinal bromine in the latter.[19] *Of key significance is the large difference (17 ppm) in chemical shift of the two bridgehead fluorines, which demonstrates that F_3 is endo.* Again the strong deshielding influence of a cis, vicinal bromine has come into play. The fact that **4d**, in which the exo atom at C_3 is perforce a fluorine, displays a single very high field resonance (196 ppm) confirms this surmise. Furthermore, the $J_{3,4}$'s in **4a** and **5**, both trans coupling constants, are virtually identical and substantially smaller than $J_{1,2}$ in **5**, a cis coupling constant. Incidentally, the large disparity (10–13 Hz) between the three-bond and four-bond coupling constants connecting vinyl with bridgehead fluorines permits assignment of the individual vinyl fluorines in **4a** as shown in Figure 1, again by analogy to **5**.

Chemistry of the Bicyclic Ketones (3) and Their Hydrates (4). Photolysis. England's finding that hexafluorocyclobutanone photodecarbonylates quantitatively to hexafluorocyclopropane[14,20] suggested that ultraviolet irradiation of **3d**, for example, should give 5*H*-pentafluorobicyclo[2.1.0]-2-pentene (**6**). This fragile molecule



3d 6 7

would undoubtedly isomerize very readily to the 5*H*-cyclopentadiene (**7**),[21] an unknown molecule when this work was done and still not easily available.[22] Photolysis in the gas phase with a medium-pressure mercury arc yielded a cyclopentadiene as we had hoped, but it was the wrong isomer: 1*H*-pentafluorocyclopentadiene (**8**)! We surmised that the desired 5*H* isomer had almost certainly formed, but that it had suffered a [1,5]-sigmatropic shift of fluorine under the reaction conditions to give essentially irreversibly the 1*H* isomer.[3b,23] Substantially greater

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[15] Perchloryl fluoride is an electrophilic fluorinating agent which has been used for α-fluorination of ketones through their enolates. Gerstenberger, M. R. C.; Haas, A. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 647–667.

[16] Middleton, W. J.; Bingham, E. M. *J. Am. Chem. Soc.* **1980**, *102*, 4845–4846.

[17] All chemical shifts reported in this paper are given in ppm upfield from internal trichlorofluoromethane (Freon 11).

[18] The coupling constants for **5** are from Cavalli (Cavalli, L. *J. Chem. Soc. B* **1970**, 1616–1623), but we agree with the chemical shifts and assignments made by Haszeldine's group.[11] Since their chemical shifts were reported relative to external trifluoroacetic acid, we have added 78.6 ppm for comparison with ours; the spectrum was apparently measured on a neat mixture of **5** and its exo, cis isomer.

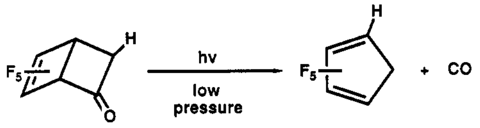
[19] Examples of this effect are found in ref 11 and in Barefoot, A. C., III; Saunders, W. D.; Buzby, J. M.; Grayston, M. W.; Lemal, D. M. *J. Org. Chem.* **1980**, *45*, 4292–4295.

[20] Phillips, D. *J. Phys. Chem.* **1966**, *70*, 1235.

[21] Andrews, G. D.; Baldwin, J. *J. Am. Chem. Soc.* **1977**, *99*, 4853 and references therein.

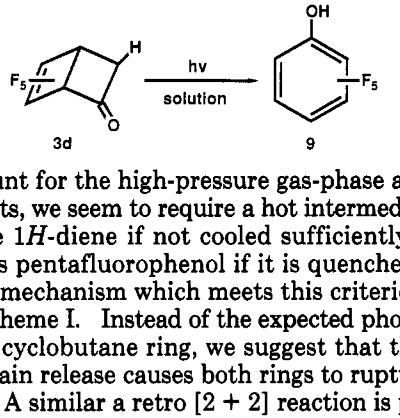
[22] Seppelt has synthesized this compound very neatly, albeit in low yield. Paprott, G.; Lentz, D.; Seppelt, K. *Chem. Ber.* **1984**, *117*, 1153–1160. Paprott, G.; Seppelt, K. *J. Am. Chem. Soc.* **1984**, *106*, 4060–4061.

stability for the 1*H* compound could be predicted with confidence on the basis of the *gem*-difluoro effect[24] (the pronounced bond-strengthening effect which accompanies the accumulation of fluorines on a carbon). Since ring-opening of the putative bicyclopentene intermediate would be highly exothermic and the lifetime between molecular collisions was long at the low pressures employed, the sigmatropic shift idea seemed eminently reasonable.[25]



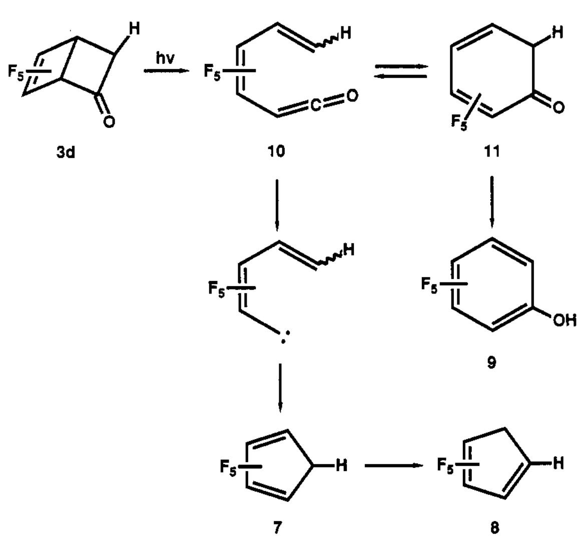
3d 8

The photolysis was repeated in the presence of 1 atm of nitrogen. It was expected that this bath gas would collisionally deactivate vibrationally excited 5*H*-cyclopentadiene, thus allowing it to survive. We were surprised to find that the product was roughly half pentafluorophenol (**9**), the other half being the 1*H*-cyclopentadiene. Apparently the collisional deactivation attempt had worked partially, but a new mechanism was required to explain the formation of pentafluorophenol. In order to cool hot intermediates more effectively, the photolysis was carried out in solution. Acetonitrile, carbon tetrachloride, and acetone were used as solvents, the first because it is transparent and resistant to atom abstraction reactions, the second because it is nonpolar, and the third because it is a triplet sensitizer. A Pyrex-filtered medium-pressure mercury arc, the full arc, and low-pressure mercury lamps were all tried as light sources. All combinations of conditions for liquid-phase photolysis gave pentafluorophenol as the principal product. Though small amounts of unidentified byproducts were formed, neither cyclopentadiene was detected.



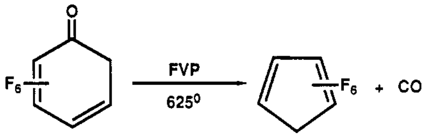
3d 9

Scheme I



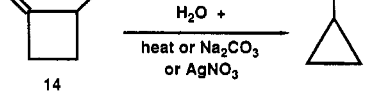
To account for the high-pressure gas-phase and liquid-phase results, we seem to require a hot intermediate which goes to the 1*H*-diene if not cooled sufficiently fast, but which gives pentafluorophenol if it is quenched quickly. A possible mechanism which meets this criterion is presented in Scheme I. Instead of the expected photocleavage of a single cyclobutane ring, we suggest that the driving force of strain release causes both rings to rupture, giving ketene **10**. A similar a retro [2 + 2] reaction is prominent in the photochemistry of the parent cyclobutanone,[26] even without the added driving force provided by a second small ring. Since difluoroketene apparently fragments to difluorocarbene and carbon monoxide even in refluxing ether,[27] it is plausible that the monofluoroketene **10** should decarbonylate if it were sufficiently hot vibrationally. The resulting carbene could cyclize to 5*H*-pentafluorocyclopentadiene (either directly or via a vinylcyclopropene), born hot enough to suffer the [1,5]-fluorine shift required to produce the observed 1*H* isomer. A more facile process would be available to ketene **10**, however: electrocyclization to 6*H*-pentafluoro-2,4-cyclohexadienone (**11**),[28] tautomerization of which would give the phenol **9**. We propose that the hot ketene cyclizes *reversibly* to the dienone and that the quenching of either molecule forestalls decarbonylation. Thermodynamically favorable as it is, (unimolecular) tautomerization of the dienone should be impeded by a rather high barrier.[29]

This scheme for the photolysis of **3d** is supported by our finding that thermolysis of highly fluorinated 2,4-cyclohexadienones gives good yields of cyclopentadienes. In fact, a new synthesis of hexafluorocyclopentadiene (**13**) has been developed based on flash vacuum pyrolysis of the perfluorodienone (**12**).[6a] In any event, if our interpretentation of the photochemistry of **3d** is correct, it is clear that the ketene decarbonylation reaction is more easily quenched by collisional cooling than is the sigmatropic shift of fluorine in the 5*H*-cyclopentadiene, for that diene was never detected under any set of reaction conditions. We regard as unlikely the possibly that the 5*H*- → 1*H*-cyclopentadiene isomerization is a fluoride ion catalyzed process, as discussed later in connection with pyrolysis experiments, but we have not excluded that mechanism. Photolysis of chloro ketone **3b** was also examined briefly in the gas phase, but only a polymeric product was obtained.



12 13

Reaction under Favorskii Conditions. Treatment of 2-bromocyclobutanone (**14**) with boiling water, hydroxide ion, or aqueous silver nitrate gives cyclopropanecarboxylic acid in high yield via the hydrated form of the ketone.[30,31]



14

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[23] For other examples of apparent [1,5]-sigmatropic shifts of fluorine in cyclopentadienes, see: reference 6a and the discussion which follows.

[24] 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.

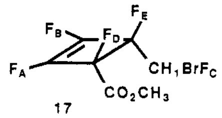
[25] Remarkably, ring opening of 5-methylbicyclo[2.1.0]-2-pentene is followed by [1,5]-sigmatropic shift of hydrogen *even in solution*.[21]

[26] Turro, N. J.; Southam, R. M. *Tetrahedron Lett.* **1967**, 545–551 and references therein.

[27] Krespan, C. G.; England, D. C. *J. Org. Chem.* **1968**, *33*, 816–821.

[28] Quinkert, G. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 790–800.

[29] The only geometrically favorable pathway is a suprafacial [1,3]-sigmatropic shift, which is, of course, orbital-topology-forbidden. Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781–932.



17

Chemical Shifts (ppm)

A	B	C	D	E
119.2	121.3	151.7	167.2	169.1

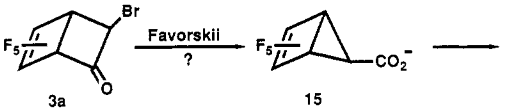
Coupling Constants (Hz)

AB	AC	AD	AE	BC	BD
12.5	3.5	6.6	5.7	1.8	4.9

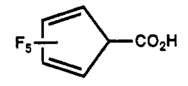
BE	CD	CE	CH_1	DE	EH_1
7.4	1.2	26	46	11.1	15.8

Figure 2. ^{19}F NMR data for cyclobutenecarboxylic acid **17**.

Bromo ketone **3a** as its hydrate **4a** might be expected by analogy to ring contract to a bicyclo[2.1.0]pentene (**15**), precursor for pentafluorocyclopenta-2,4-dienecarboxylic acid (**16**). The latter was of interest as a potential source of other 5-substituted pentafluorocyclopentadienes.

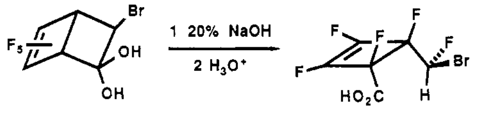


3a 15



16

In the event, hydrate **4a** failed to react with water over a period of several days, but it was attacked rapidly by 20% sodium hydroxide. After acidification, 1,2,3,4-tetrafluoro-4-(bromofluoromethyl)cyclobut-2-enecarboxylic acid (**17**) was obtained in high yield, as determined by ^{19}F NMR spectroscopy. Close examination of the ^{19}F NMR spectrum of **17** revealed that no diastereomers were present and thus that the ring opening reaction is stereospecific. This highly hygroscopic acid was difficult to purify, so the corresponding methyl ester (**18**) was prepared by reaction of **17** with diazomethane and purified by preparative gas-liquid chromatography.



4a 17

The NMR coupling constants for **17** were determined with the help of spin decoupling and computer simulation. These values and the chemical shift assignments (acetonitrile-d_3) appear in Figure 2, where fluorines are labeled A, B, ... in order of increasing shielding. The two lowest field fluorines have appropriate chemical shifts for vinyl fluorines on a cyclobutene ring, and the presence of that structural element is confirmed by a C=C stretching band at 1790 cm^{-1} in the infrared spectrum. Which vinyl fluorine is F_A and which F_B is not certain; they have been assigned as shown by comparison of their coupling constants to F_D and F_E with corresponding couplings in **25**, to be discussed. F_C is clearly identified by the large and characteristic coupling to the geminal proton. F_D and F_E are distinguished by the large coupling of the latter both to F_C and to H_1.[32]

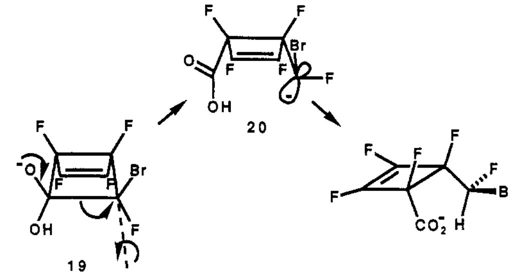
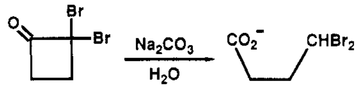


Figure 3. Proposed stereochemistry of ring cleavage.

As indicated in **17**, we believe that ring cleavage occurs with retention of configuration at C_3. The principal evidence for that surmise is presented later in a discussion of the degradation of acid **17** by strong base. At least two factors can be identified which help to explain the retention of configuration. The presence of fluorine and bromine at the incipient carbanion center should substantially increase the barrier to inversion.[33] Furthermore, less geometric change is required to maximize stabilization of the developing carbanion by negative hyperconjugation with the C_4 fluorine[34] if configuration is retained than if it is inverted. The presumably optimal antiperiplanar conformation **20**[35] shown in Figure 3 can be achieved by rotation through ~60° about the C_3–C_4 bond as anion **19** opens up. Whether this geometry is reached before protonation takes place is not known, of course, nor is it known whether the new carboxyl group provides the proton directly.

We reasoned that ring contraction would be favored relative to ring opening, which does not involve cleavage of the C–Br bond, if a strong enough "pull" could be exerted on the bromine atom. Nonetheless, reaction of hydrate **4a** with aqueous silver nitrate gave **17** in about 50% conversion after 1 day at room temperature, and there was no evidence of ring-contracted product. Clearly silver ion catalysis was effective, presumably through complexation of the bromine atom, even though the "wrong" product was obtained. Apparently this complexation stabilizes by the inductive and field effects the carbanion which is developing in the ring-cleavage transition state.

Several factors may contribute to the preference for ring opening of **4a** over ring contraction. The former process is *favored* by the release of ring strain and by halogens on and near the developing carbanion. Indeed, cyclopropanecarboxylic acids are not produced and ring opening is the major reaction pathway when α,α-dihalocyclobutanones such as **21** are subjected to Favorskii conditions,[36] principally because of the additional stability conferred on the developing carbanion by a second halogen.



21

Ring contraction of **4a** is *disfavored* by the rigid skeleton which makes ideal transition-state geometry inaccessible,

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(30) Conia, J. M.; Ripoll, J. L. *Bull. Soc. Chim. Fr.* **1963**, 755–763. Rappe, C.; Knutsson, L. *Acta Chem. Scand.* **1967**, *21*, 163–167. Conia, J. M. *Tetrahedron Lett.* **1963**, 1175–1177.

(31) For a general discussion of reactions of this type, see: Conia, J. M.; Salaun, J. R. *Acc. Chem. Res.* **1972**, *5*, 33–40.

(32) For the ^{19}F NMR spectra of model compounds, see: (a) Newmark, R. A.; Apai, G. R.; Michael, R. O. *J. Magn. Reson.* **1969**, *1*, 418–431. (b) Harris, R. K.; Ditchfield, R. *Spectrochim. Acta* **1968**, *24A*, 2089–2105. (c) Banks, R. E.; Barlow, M. G.; Deem, W. R.; Haszeldine, R. N.; Taylor, D. R. *J. Chem. Soc. C* **1966**, 981–984.

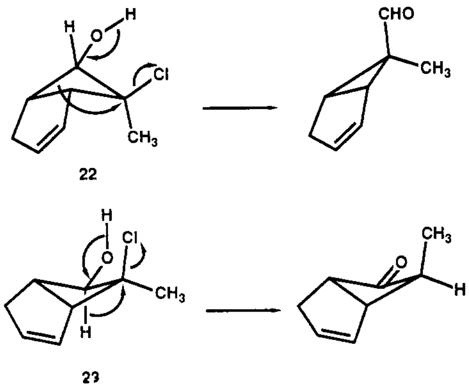
(33) Halogen substituents dramatically increase pyramidal inversion barriers in amines, for example. Lambert, J. *Top. Stereochem.* **1971**, *6*, 19–105.

(34) Farnham, W. B.; Dixon, D. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1988**, *110*, 2607–11 and references therein.

(35) Rahman, M. M.; Lemal, D. M.; Dailey, W. P. *J. Am. Chem. Soc.* **1988**, *110*, 1964–6 and references therein.

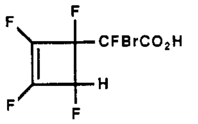
(36) Conia, J. M.; Salaun, J. R. *Acc. Chem. Res.* **1972**, *5*, 33–40.

Scheme II



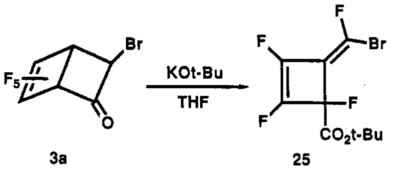
by the presence of destabilizing fluorines on the developing cyclopropane ring,[37] by the homoantiaromaticity characteristic of bicyclo[2.1.0]pentenes,[38] and by the diminished ease of S_N2 displacement of a bromine situated geminal to another halogen.[39] For ideal transition-state geometry, the migrating bond and the bond to the leaving group should be antiperiplanar. The reactions of 7-chlorobicyclo[3.2.0]-2-hepten-6-ols **22** and **23** with aqueous potassium hydroxide illustrate the strict conformational requirements of the Favorskii rearrangement (Scheme II).[36]

A priori, one might have expected ring opening to occur by scission of the C_1–C_2 bond, as the developing carbanion in this case would enjoy allylic stabilization. The resulting cyclobutenylacetic acid structure **24** is reasonably consistent with our ^{19}F NMR and infrared data, but it can be ruled out with confidence on chemical grounds. Degradation by strong base of the acid obtained under Favorskii conditions yields a product which could originate only from structure **17**, as discussed below.

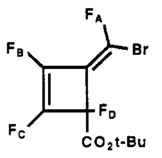


24

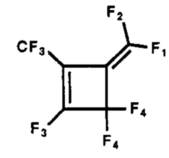
Reaction in Aprotic Media. Potassium *tert*-butoxide in tetrahydrofuran transformed bromo ketone **3a** into a new type of cleavage product, the very labile methylenecyclobutenecarboxylic ester **25**. Only a single set of four resonances was observed in the ^{19}F NMR spectrum, indicating once again a stereospecific process. Attempts to purify this compound were unavailing, but evidence for its structure was provided by its ^{19}F NMR spectrum and by derivatives of **25** to be described.



^{19}F NMR spectral data for **25** are presented in Figure 4, together with relevant coupling constants for the model compound **26**.[32c] The chemical shifts are in good agreement with the proposed structure; particularly revealing is the lowest field signal (89.8 ppm), which is characteristic of a *terminal* vinyl fluorine. In **26**, for example, F_1 and F_2 appear at 91.3 and 96.8 ppm, respectively. The largest F–F coupling constant in highly fluorinated 1,3-dienes, usually 20–25 Hz, connects fluorine at opposite ends of the unsaturated system.[32a,40] Figure 4 indicates closely agreeing values in this range for J_{AC} in **25** and the corresponding $J_{2,3}$ in **26**. The exocyclic double bond *configuration* in **25** was assigned on the basis of mechanistic considerations presented below, as the spectroscopic evidence is inconclusive. For the opposite configuration, the match of J_{AC} with its counterpart in **26** ($J_{1,3}$) is not quite as good as with $J_{2,3}$, but that of J_{AD} with $J_{1,4}$ is better than with $J_{2,4}$ (Figure 4).



25



26

Chemical Shifts for 25

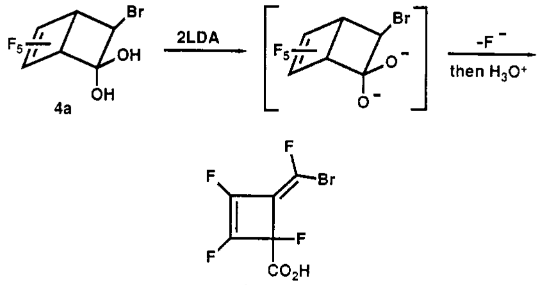
A	B	C	D
89.8	113.8	127.6	171.2

Coupling Constants (Hz)

25	AB 6.2	AC 20.0	AD 0.7	BC 10.0	BD 4.5	CD 6.1
26		2,3 22.6	2,4 2.8			3,4 8.5
		1,3 25.1	1,4 1.3			

Figure 4. ^{19}F NMR data for diene **25** and model compound **26**.

In a transformation parallel to the *tert*-butoxide reaction above, treatment of hydrate **4a** with lithium diisopropylamide gave (after acidification) the carboxylic acid (**27**) corresponding to **25**.



Formation of **25** and **27** is imagined to proceed analogously to the ring cleavage reaction in protic media (Figure 3), except that the transient carbanion which is generated eliminates the β-fluorine since no proton source is available. The reaction stereochemistry is thus controlled by the factors discussed earlier, with elimination of fluoride ion taking place via an antiperiplanar transition state.[41,42]

When cyclobutenecarboxylic acid **17** was subjected to the action of excess lithium diisopropylamide, diene acid **27** was again formed. This finding constitutes strong evidence that **17** has the assigned stereochemistry. If it had the opposite configuration at the protonated carbon, it should give upon elimination a product with double-bond configuration opposite that of **27**.

Since acid **27**, like **25**, was sensitive and very difficult to purify, it was esterified with diazomethane. Though

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[37] See, for example, Dailey, W. D.; Lemal, D. M. *J. Am. Chem. Soc.* **1984**, *106*, 1169–1170.

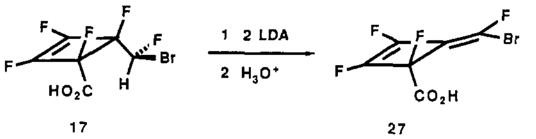
[38] Roth, W. R.; Klärner, F.-G.; Lennartz, H.-W. *Chem. Ber.* **1980**, *113*, 1818–1829. Andrews, G. D.; Baldwin, J. E.; Gilbert, K. E. *J. Org. Chem.* **1980**, *45*, 1523–1524.

[39] Hine, J. *Physical Organic Chemistry*, 2nd. ed.; McGraw-Hill: New York, 1962; pp 173–176.

[40] Servis, K. L.; Roberts, J. D. *J. Am. Chem. Soc.* **1965**, *87*, 1339–1344.

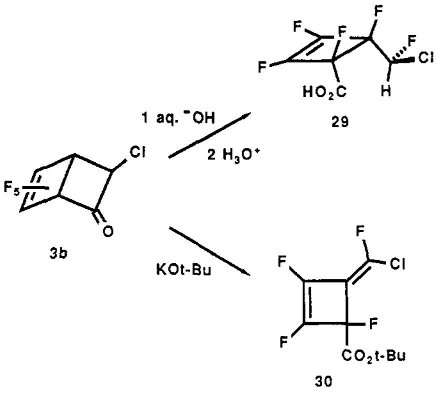
[41] Saunders, W. H.; Cockerill, A. F. *Mechanisms of Elimination Reactions*; John Wiley and Sons: New York, 1973.

[42] See the discussion of the β-fluoroethyl anion In Schleyer, P. v. R.; Kos, A. J. *Tetrahedron* **1983**, *39*, 1141–50.

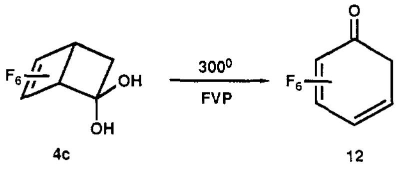


white crystals of the methyl ester (**28**) could be obtained by vacuum sublimation, the compound soon polymerized to a tough plastic even under nitrogen. Its mass spectrum confirmed the expected molecular weight and revealed an appropriate fragmentation pattern for structure **28**. The infrared spectrum (vapor) showed intense double-bond stretching bands at 1775 and 1750 cm^{-1}.

Chloro ketone **3b** displayed reactivity parallel to that of **3a**. Treatment with aqueous sodium hydroxide gave cyclobutenecarboxylic acid **29**, while potassium *tert*-butoxide transformed **3b** into diene **30**. The ^{19}F NMR spectra of **29** and **30** were strikingly similar to those of **17** and **25**, respectively. These chloro compounds were not characterized further.



Pyrolysis. Thermal behavior was explored with two representatives from the series of ketones and their hydrates. Flash vacuum pyrolysis of perfluorohydrate **4c** at 300 °C resulted in dehydration and ring opening, giving exclusively and in high yield hexafluorocyclohex-2,4-dienone (**12**).[6a] As noted earlier, **12** undergoes further reaction when subjected to flash vacuum pyrolysis at 625 °C, decarbonylating to produce hexafluorocyclopentadiene (**13**) in good yield.[6a] Thus, **13** can be synthesized from hydrate **4c** in a single step. Since we are able to prepare dienone **12** in one step from pentafluorophenol, albeit contaminated with its 2,5-isomer, the route to **12** described here is unlikely to be useful synthetically. The general approach represented by the **4** → **12** reaction may find application, however, in the synthesis of highly fluorinated cyclohexa-2,4-dienones whose direct preparation from the phenol gives a preponderance of the wrong isomer and/or isomer separation is difficult.[43]



Chloro ketone **3b** was subjected to flash vacuum pyrolysis at 650 °C and 0.1 Torr. Under these conditions ring opening to dienone **31** was followed directly by decarbonylation, producing chlorocyclopentadienes. The initially formed 5-chloropentafluorocyclopentadiene (**32**) was unstable with respect to the 1-chloro (**33**) and 2-chloro (**34**) isomers because of the *gem*-difluoro effect, and it isomerized completely to these compounds under the reaction conditions.[3a,6a] Cyclopentadienes **33** and **34** were obtained in the ratio 2.3:1, which was shown to be the equilibrium composition under the reaction conditions. Consistent with the above interpretation, the same product composition was obtained by flash vacuum pyrolysis of dienone **31** at the temperature chosen for chloro ketone **3b**. We were unable to find pyrolysis conditions for **31** which were both vigorous enough to generate cyclopentadienes yet sufficiently mild to leave the 5-chloro isomer intact.

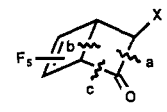
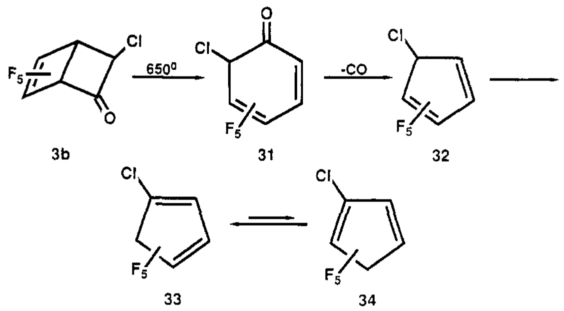


Figure 5. Modes of cleavage of the bicyclohexenones.



Reminiscent of the behavior described earlier of 5*H*-pentafluorocyclopentadiene formed by photolysis of **3d**, the 5-chloro compound may have suffered sequential [1,5]-sigmatropic shifts of fluorine to generate first **33** and then **34**. While we regard this as the most likely mechanism for isomerization, we cannot conclusively rule out surface catalysis.[44] Indeed, our observation that a few percent of hexafluorobenzene accompanied by cyclopentadienes in the pyrolysis product indicates that the chemistry occurring in the pyrolysis tube was not exclusively unimolecular.

Conclusion. Readily prepared in three steps from hexafluorobenzene, 3-substituted pentafluorobicyclo[2.2.0]-5-hexen-2-ones have been found to undergo several different types of ring-cleavage reactions. Under Favorskii conditions, scission of bond a in Figure 5 occurred with the formation of cyclobutenecarboxylates. In aprotic media, basic reagents effected both cleavage at bond a and fluoride elimination, leading to methylenecyclobutenecarboxylates. Pyrolysis caused opening of the central bond b with the formation of 2,4-cyclohexadienones, which at higher temperatures suffered decarbonylation to give cyclopentadienes. Photolysis results for the 3-hydro derivative (the only well-studied example) are best interpreted in terms of initial scission of both bonds a and b, yielding ultimately a cyclopentadiene or pentafluorophenol in a highly pressure-dependent transformation. The thermal and photochemical transformations which gave cyclopentadienes entailed at some stage cleavage of bond c.

Experimental Section

The ^{19}F NMR spectra were obtained on a JEOL FX-60Q Fourier transform instrument operating at 56.2 MHz or on a Varian XL-300 Fourier transform spectrometer operating at 282.2

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[43] Dienone 12 and its 2,5-isomer differ in boiling point by 3 °C. Isomer separation can be complicated by the fact that such highly electron-deficient dienones are very reactive; 12 is readily attacked by residual pentafluorophenol, for example.[6a]

[44] For a discussion of the problems in establishing the mechanism(s) of fluorine migration in cyclic diene pyrolyses, see: Feast, W. J.; Morland, J. B. *J. Fluorine Chem.* **1981**, *18*, 57–73. Burdon, J.; Childs, A.; Parsons, I. W.; Rimmington, T. W. *J. Fluorine Chem.* **1981**, *18*, 75–85.

MHz. Chemical shifts are reported in ppm upfield from internal trichlorofluoromethane (Freon 11). Mass spectra were measured by Rudy Zsolway on a Finnigan GC/EI-CI 4000 spectrometer. Analytical gas–liquid chromatography was carried out with a Hewlett-Packard 5880A gas chromatograph using a flame ionization detector. Peak areas were determined by electronic integration and are uncorrected for differential detector response. Preparative GC was done with a Hewlett-Packard 5750 chromatograph using a thermal conductivity detector. Melting points were determined in sealed Pyrex capillaries and are uncorrected. The term "static" vacuum transfer refers to a closed system distillation, while "dynamic" vacuum transfers were done by pumping a sample to or through a cold trap. Vacuum transfers were carried out from room temperature to −196 °C unless noted otherwise.

Pyrolysis tubes were prepared by wrapping a coil of nichrome wire (22 gauge, 1 ohm/ft, Ogden Mfg. Co.) around fused quartz tubing. An iron-constantan thermocouple was placed against the outside of the tube in the center of the zone to be heated, without touching the nichrome wire. The entire tube was then insulated with three layers of asbestos tape. Temperatures were controlled with variacs and were monitored by a 1000 °C temperature readout (Omega Engineering).

All compounds were prepared under nitrogen (dried with a train containing concentrated sulfuric acid, potassium hydroxide, and Drierite) except when indicated otherwise. All solvents and reagents were reagent grade, and solvents were dried according to literature procedures.[45] Hexafluorobenzene was purchased from the Fairfield Chemical Co.; trifluoromethyl hypofluorite and Freon 11 from PCR Research Chemicals, Inc.; perchloryl fluoride from Ozark-Mahoning, a division of Pennwalt. Microanalyses were carried out by Galbraith Laboratories, Knoxville, TN.

Hexafluorobicyclo[2.2.0]hexa-2,5-diene (1). This diene was prepared in 90% yield by photorearrangement of hexafluorobenzene (10.5 g, 56.5 mmol) as described by Dailey et al.[46] and dynamically transferred to a liquid nitrogen cooled trap containing 20 mL of dry, degassed THF. **Warning**: the Dewar benzene is unstable in the liquid state and is apt to explode unpredictably. However, we have handled solutions of the compound in concentrations up to 30% without incident over a period of years.

2-*tert*-Butoxypentafluorobicyclo[2.2.0]hexa-2,5-diene (2). To hexafluorobicyclo[2.2.0]hexadiene (1) (29.9 g, 0.161 mol) in 60 mL of dry THF was added another 60 mL of dry THF in a flame-dried, 500-mL three-necked flask equipped with paddle stirrer and pressure-equalizing dropping funnel under an atmosphere of nitrogen. Freshly made and sublimed potassium *tert*-butoxide (20.6 g, 0.184 mol, 1.1 equiv), handled in a nitrogen-filled glovebox, was dissolved in 100 mL of THF and dripped into the vigorously stirred Dewar benzene solution at −23 °C (CO_2 slush bath). The addition was complete in 2.75 h, and after an additional half hour at that temperature the brown-black mixture was suction filtered through a bed of filter aid. The clear yellow filtrate was set aside, and the black ooze on the filter was stirred with 50 mL of methylene chloride and again suction filtered. The THF was distilled at 100–110 mm with the pot at 25 °C or below, and the methylene chloride fraction was also stripped in the cold. The combined residues were distilled at lower pressure to give two fractions collected in dry ice cooled receivers: Fraction 1, bp 25–27 °C (0.1 m), 10.55 g (55% ether, 5.8 g, 24 mmol); Fraction 2, bp 30–31 °C (0.1 mm), 15.66 g, 62 mmol (~95% pure). Total corrected yield was 53%; typical yields are 50–60%. GC (column, 12.5 ft × $^1/_8$ in., 5% SF-96 on Chromosorb-W HP; oven, 70 °C; flow, 20 mL/min; injector, 130 °C): t_R 3.75 min; IR (CCl_4) 3000 (ν_{C-H}), 1750 and 1710 ($\nu_{C=C}$), 1330 cm^{-1} (ν_{CF}); MS *m/e* 240 (M^+), 57 (base, $C_4H_9^+$). Anal. Calcd for $C_{10}H_9F_5O$: C, 49.96; H, 3.77. Found: C, 49.91; H, 3.83.

***exo*-3-Bromopentafluorobicyclo[2.2.0]hex-5-ene-2,2-diol (4a).** Bromine was added dropwise to the *tert*-butyl ether **2** (1.164 g, 4.85 mmol) in 10 mL of dry *o*-dichlorobenzene (distilled and stored over 4-Å molecular sieves) at 0 °C until a light orange color persisted. This solution was degassed and pumped (0.015 mm) through three dry U-traps in series at −15, −60, and −196 °C during 3 h. The second, filled with glass helices, caught 3-bromopentafluorobicyclo[2.2.0]hex-5-en-2-one and *tert*-butyl bromide. The first trap contained *o*-dichlorobenzene and minor amounts of ketone. The third trap had *tert*-butyl bromide, hydrogen bromide, and bromine. **Warning**: this trap may present an explosion hazard if unvented when warmed to room temperature. The contents of trap two were statically transferred onto 87 μL (1 equiv) of distilled, degassed water at −196 °C. After four freeze–thaw cycles the *tert*-butyl bromide was statically transferred to leave behind 0.925 g (68% yield) of white, crystalline hydrate (mp 55–57 °C). Maintaining this hydrate for 1 h at 0.015 mm left analytically pure 3-bromopentafluorobicyclo[2.2.0]hex-5-ene-2,2-diol: mp 61–61.4 °C (sealed capillary); IR (KBr) 3440 (ν_{O-H}), 1755 ($\nu_{C=C}$), 1318 cm^{-1} (ν_{CF}); MS *m/e* 262 ($M^+ - H_2O$), 234, 215, 45 (base). Anal. Calcd for $C_6H_2BrF_5O_2$: C, 25.65; H, 0.72; Br, 28.43; F, 33.81. Found: C, 25.74; H, 0.77; Br, 27.89; F, 33.92.

***exo*-3-Bromopentafluorobicyclo[2.2.0]hex-5-en-2-one (3a).** A solution of hydrate **4a** (0.65 g, 2.3 mmol) in 50 mL of *o*-dichlorobenzene was degassed and then efficiently stirred for 25 min with a 10-fold excess (by volume) of phosphorus pentoxide. Volatiles were then pumped into two dry traps at −15 and −78 °C (helix-packed) during 2 h. The second trap contained clear, colorless, highly mobile, liquid ketone (0.60 g, 2.3 mmol, 100% yield): IR (vapor) 1850 ($\nu_{C=O}$), 1755 ($\nu_{C=C}$), 1485 (w), 1370 and 1350 (ν_{CF}), 1270, 1165 cm^{-1}.

***exo*-3-Chloropentafluorobicyclo[2.2.0]hex-5-en-2-one (3b).** Chlorine was slowly bubbled into a solution of *tert*-butyl ether **2** (1.24 g, 5.18 mmol) in 10 mL of *o*-dichlorobenzene at 0 °C. The reaction was complete when the bright yellow color of chlorine persisted for several minutes. This solution was degassed, and 1.5 mL of phosphorus pentoxide was added via a solids addition funnel. After the mixture had been stirred for 5 min, volatiles were pumped into three dry traps at −15, −60, and −196 °C. Trap two contained clear and colorless chloro ketone (0.796 g, 70% yield). IR analysis of the contents of the −196 °C trap showed *tert*-butyl chloride, chlorine, and hydrogen chloride. **Warning**: this trap presents an explosion hazard if allowed to warm unvented. IR of **3b** (vapor): 1850 ($\nu_{C=O}$), 1750 ($\nu_{C=C}$), 1370 and 1350 (ν_{CF}), 1280, 1238, 1160, 1000 cm^{-1}.

***exo*-3-Chloropentafluorobicyclo[2.2.0]hex-5-ene-2,2-diol (4b).** Onto distilled water (13.1 μL) was statically transferred chloro ketone **3b** (0.159 g, 0.728 mmol). This mixture was frozen and thawed six times and then maintained for 30 min at 0.02 mm. Analytically pure, white chlorohydrate remained (0.138 g, 0.584 mmol, 80% yield): mp 67–68 °C; IR (*o*-dichlorobenzene) 3320 (ν_{OH}), 1755 ($\nu_{C=C}$), 1370 cm^{-1} (ν_{CF}); MS *m/e* 218 ($M^+ - H_2O$), 45 (base). Anal. Calcd for $C_6H_2ClF_5O_2$: C, 30.47; H, 0.85; Cl, 14.99; F, 40.16. Found: C, 30.32; H, 0.92; Cl, 14.84; F, 40.21.

Hexafluorobicyclo[2.2.0]hex-5-ene-2,2-diol (4c). A solution of Dewar benzene **2** (4.75 g, 19.7 mmol) in 50 mL of methylene chloride was cooled to −78 °C in a special cylindrical reactor having an inlet tube just above the surface of the liquid for purging with nitrogen. **CAUTION**: when this reaction was run at 0 °C in a conventional reactor the gases above the solution detonated with great force and a brilliant flash. This probably resulted from a mixture of trifluoromethyl hypofluorite with isobutene.

Trifluoromethyl hypofluorite (4.68 g, 44.0 mmol) was bubbled through the stirred solution for 3 h at −78 °C while a slow stream of nitrogen purged the head space, exiting through a bubbler. Upon warming to room temperature the reaction mixture effervesced for about 0.5 h. After the gaseous emission subsided the solvent was distilled at 110 mm, heated by an oil bath at 25–30 °C. The remaining brown, flaky residue was dynamically transferred (0.1 mm) with heating to 30 °C into a U trap at −78 °C. The resulting off-white crystalline mixture was largely hydrate **4c** (2.51 g, 11.4 mmol, 58%) together with a small quantity of *exo*-3*H*-pentafluorobicyclo[2.2.0]-hex-5-ene-2,2-diol (**4d**) (5%): IR (KBr) 3390 (ν_{OH}), 1755 cm^{-1} ($\nu_{C=C}$). Recrystallizations from benzene, methylene chloride, and hexanes resulted in increased tar formation without significant purification. Repeated trap-to-trap dynamic vacuum sublimations (0.01 mm) in each instance initially produced white crystals, leaving behind a brown residue. The crystals turned brown in vacuo at −10 °C, and the rate was much greater at room temperature. Unlike the 3-chloro- and 3-bromopentafluorobicyclo[2.2.0]hex-5-ene-2,2-diols, this com-

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

pound did not dehydrate at room temperature with phosphorus pentoxide in acetonitrile-d_3.

***exo*-3*H*-Pentafluorobicyclo[2.2.0]hex-5-en-2-one (3d).** *tert*-Butyl ether **2** (0.151 g, 0.63 mmol) was dissolved in 50 mL of dry *o*-dichlorobenzene, and concentrated sulfuric acid was added. When the mixture had been stirred for 15 min, the system was evacuated through a pair of traps, the first at 0 °C and the second at −78 °C. The first trap collected only dichlorobenzene, and the second collected the liquid ketone along with a small amount of crystals of its hydrate **4d**. The ketone was vacuum-transferred into a storage bulb (0.096 g, 0.52 mmol, 85% yield).

Photolysis of *exo*-3*H*-Pentafluorobicyclo[2.2.0]hex-5-en-2-one (3d). Vapor Phase. Ketone **3d** (20 mg, 0.11 mmol) was vacuum transferred into a 250-mL quartz round-bottom flask. The flask was exposed to the full mercury arc (water-cooled Hanovia 450-W medium-pressure lamp) at a distance of 10 cm for 20 min. Product was vacuum-transferred into an NMR tube containing acetonitrile, and its ^{19}F NMR spectrum revealed its identity as 1*H*-pentafluorocyclopentadiene.[3b] The photolysis was repeated with 1 atm of nitrogen present, and the product was now found to be a roughly equimolar mixture of 1*H*-pentafluorocyclopentadiene and pentafluorophenol. The latter was identified by comparison of its ^{19}F NMR spectrum with that of an authentic sample (Aldrich Chemical Co.). ^{19}F NMR (1:1 CH_3CN/CD_3CN) (1*H*-pentafluorocyclopentadiene) 123.9 (m), 131.0 (m), 152.5 (m), 160.8 ppm (m); (pentafluorophenol) 163.1 (m), 165.8 (t), 171.4 ppm (t).

Liquid Phase. Solutions of the ketone were prepared by vacuum transferring a small portion (usually 20 mg) of the ketone into an NMR tube containing the solvent and a small amount of trichlorofluoromethane. Pyrex tubes were used for Pyrex-filtered photolyses, and quartz tubes used for full mercury arc and 2537 A photolyses. Full-arc photolyses were performed with the Hanovia lamp described above at a distance of 3 cm for 20 min. Pyrex-filtered photolyses were performed with the same apparatus with a Pyrex sleeve surrounding the lamp. Separate photolyses were carried out with each of the three light sources using each of three solvents: acetone, acetonitrile, and carbon tetrachloride. In all cases, the major product was pentafluorophenol; small amounts of other materials were not identified. No cyclopentadiene was observed.

1,2,3,4-Tetrafluoro-4-(bromofluoromethyl)cyclobut-2-enecarboxylic Acid (17). A. To 1.2 g (4.3 mmol) of *exo*-3-bromo-2,2-dihydroxypentafluorobicyclo[2.2.0]hex-5-ene (**4a**) in 5 mL of *o*-dichlorobenzene was added dropwise 2 mL of 20% sodium hydroxide. After being stirred for ~0.5 h, the resulting suspension was extracted twice with 10 mL of ether, made strongly acidic with 50% sulfuric acid, and then reextracted with four 10-mL portions of ether. The ether was statically transferred from the cyclobutenecarboxylic acid to yield 1.16 g (~90% yield) of a viscous brown oil: IR (CCl_4) 1790 ($\nu_{C=C}$), 1745 ($\nu_{C=O}$), 1380 and 1360 cm^{-1} (ν_{CF}); ^{19}F NMR (CD_3CN) 117.6 (m), 120.9 (m), 150.1 (m), 166.3 (m), 167.3 ppm (m).

To a small quantity of this organic acid was added concentrated ammonium hydroxide. Removal of all excess reagent and water under vacuum yielded the ammonium salt: IR (KBr) 1790 ($\nu_{C=C}$), 1620 cm^{-1} (ν_{COO^-}).

B. To 0.05 g (0.2 mmol) of bromohydrate **4a** was added 0.07 g (0.4 mmol) of aqueous silver nitrate. After 22 h at room temperature ^{19}NMR analysis revealed a mixture containing 50% of the cyclobutenecarboxylic acid derivative and 50% starting material.

Methyl 1,2,3,4-Tetrafluoro-4-(bromofluoromethyl)cyclobut-2-enecarboxylate (18). To acid **17** (0.54 g, 1.92 mmol) in 5 mL of ether was added 4 mL of diazomethane in ether (0.48 M). After effervescence subsided the ether was distilled under nitrogen. The product ester (0.53 g, 95% yield) was then vacuum transferred; it was purified and analyzed by GC (25 m methylsilicone capillary column, 110 °C; head pressure, 15 psi; injector, 155 °C; t_R 4.8 min): IR (ether) 1780 ($\nu_{C=C}$), 1760 and 1740 ($\nu_{C=O}$), 1373 and 1350 cm^{-1} (ν_{CF}); ^{19}F NMR (ether) 119.7, 122.7, 152.0 ($J_{\text{gem-HF}}$ = 49 Hz), 166.7, 167.2 ppm; MS *m/e* 294 and 296 (M$^+$), 59 (base). Anal. Calcd for $C_7H_4BrF_5O$: C, 28.50; H, 1.37; Br, 27.08; F, 32.20. Found: C, 28.34; H, 1.42; Br, 26.80; F, 32.33.

***tert*-Butyl 1,2,3-Trifluoro-4-(bromofluoromethylene)cyclobut-2-enecarboxylate (25).** To freshly sublimed potassium *tert*-butoxide (0.262 g, 2.33 mmol) dissolved in 5 mL of degassed THF was statically transferred 3-bromopentafluorobicyclo[2.2.0]hex-5-en-2-one (**3a**) (0.574 g, 2.18 mmol). Upon warming to −78 °C, the reaction mixture turned a beautiful clear orange and on further warming to room temperature became an opaque red-brown color. Dynamic vacuum transfer for 4 h with gradual heating to about 40 °C gave a clear, slightly yellow solution of *tert*-butyl ester **25**: GC (column, 12.5 ft × $^1/_8$ in., 5% SF-96 on Chromosorb-W HP; oven initial, 100 °C; program 10 °C/min; oven final, 175 °C/10 min; injector, 190 °C) t_R 6.3 min (70% of volatiles, excluding THF). An attempt to purify this labile product by preparative GC gave material more impure than the starting ester.

1,2,3-Trifluoro-4-(bromofluoromethylene)cyclobut-2-enecarboxylic Acid (27). A. To a dry two-necked 25-mL flask containing stirred, freshly distilled diisopropylamine (0.87 g, 8.7 mmol) at −78 °C under dry nitrogen was added 5.6 mL of *n*-butyllithium in hexane (1.55 M). A solution of bromohydrate **4a** (1.1 g, 4.1 mmol) in 10 mL of THF was then added to the lithium diisopropylamide (LDA) dropwise at −78 °C. This mixture darkened to a reddish brown over 30 min. After it had warmed to room temperature, the solvents and other volatile components were removed in vacuo. The brown residue was extracted twice with 25-mL portions of ether, made strongly acidic with 20% hydrochloric acid, and extracted with four 10-mL portions of ether. The latter ether extracts were dried ($MgSO_4$) and stripped; the residue was evacuated to 0.015 mm for about 1 h to give 0.9 g of material of which about 90% (as judged from the ^{19}F NMR spectrum) was the acid **27**: IR (ether) 1760–1740 ($\nu_{C=C}$, $\nu_{C=O}$), 1370 cm^{-1} (ν_{CF}); ^{19}F NMR (ether) 90.0 (1 F), 115.3 (1 F), 127.8 (1 F), 172.3 ppm (1 F). Vacuum sublimation at 50 °C and 0.015 mm gave a white solid, which was stored overnight in a nitrogen-filled drybox. The sublimate turned a light brown during this time, and an unsuccessful attempt to scrape it from the cold finger revealed it to be a tough plastic material.

B. A solution of 1,2,3,4-tetrafluoro-4-(bromofluoromethyl)cyclobut-2-enecarboxylic acid (**17**) (0.12 g, 0.43 mmol) in 1 mL of dry *o*-dichlorobenzene was added to LDA (0.86 mmol, prepared as above) at −78 °C. This mixture turned dark red. After 1 day it was treated with 5 mL of water, extracted with ether (2 × 10 mL), made strongly acidic with concentrated sulfuric acid, and extracted again with ether. The latter ether extracts contained a mixture of starting material and the product acid **27** in a ratio of about 1:2, as determined by ^{19}F NMR spectroscopy.

Methyl 1,2,3-Trifluoro-4-(bromofluoromethylene)cyclobut-2-enecarboxylate (28). Diazomethane in ether (2 mL, 0.48 M, 0.96 mmol) was added to acid **27** (0.26 g, 0.93 mmol) in 5 mL of ether. After 15 min the yellow color of the diazomethane had disappeared: GC (column, 25 m methylsilicone capillary, 110 °C; head pressure, 15 psi; injector, 160 °C) t_R 4.36 min; IR (ether) 1760–1740 ($\nu_{C=C}$, $\nu_{C=O}$), 1370 (ν_{CF}); ^{19}F NMR (ether) 89.1 (1 F), 113.9 (1 F), 127.9 (1 F), 172.4 ppm (1 F); MS 274 (M$^+$), 167 (base). After 10 min more this mixture began to darken. Ether was gently removed by distillation under nitrogen until about 1 mL of the brown solution remained. A dynamic transfer was carried out over several hours at 0.01 mm with gentle heating to 40 °C. Initially clear and colorless, the transferred material began to darken at room temperature in vacuo within 10 min. In 12 h at −5 °C in vacuo most of the product had polymerized: ^{19}F NMR (ether) 37–189 ppm (broad signals). Dynamic vacuum transfer again gave clear and colorless methyl ester as shown by GC and ^{19}F NMR data, but it soon turned yellow. Due to its lability we were unable to purify fully the methyl 1,2,3-trifluoro-4-(bromofluoromethylene)cyclobut-2-enecarboxylate.

1,2,3,4-Tetrafluoro-4-(chlorofluoromethyl)cyclobut-2-enecarboxylic Acid (29). A. One drop of 20% sodium hydroxide was added to a sample of 3-chloropentafluorobicyclo[2.2.0]hex-5-ene-2,2-diol (**4b**) (30 mg, 0.11 mmol) in 1 mL of acetonitrile-d_3. After shaking, the mixture was made strongly acidic with 50% sulfuric acid. The yield of the cyclobutenecarboxylic acid **29** was greater than 90% based on ^{19}F NMR: IR (CD_3CN) 1790 ($\nu_{C=C}$), 1750 ($\nu_{C=O}$), 1375 cm^{-1} (ν_{CF}); ^{19}F NMR (CD_3CN) 118.5 (1 F), 120.6 (1 F), 147.2 (1 F, $J_{\text{gem-HF}}$ = 50 Hz), 165.9 (1 F), 172.6 ppm (1 F).

B. A similar experiment in which ~30% NaOD/D_2O was substituted for 20% NaOH gave after acidification 1,2,3,4-tetrafluoro-4-chlorodeuteriofluoromethyl)cyclobut-2-enecarboxylic acid: ^{19}F NMR (CD_3CN) 118.3 (1 F), 120.7 (1 F), 148.0 (1 F, $J_{\text{gem-DF}}$

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%.

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

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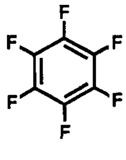
cis-5,6-Dichlorohexafluorocyclohexa-1,3-diene (*cis*-**8**) has been synthesized in five steps and 63% overall yield from hexafluorobenzene (**1**). Attempts to synthesize the bromine analogue of **8** have failed because aromatization occurs in the final, pyrolytic step. Conjugated diene *cis*-**8** 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.



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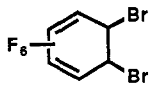
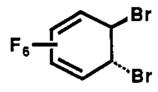
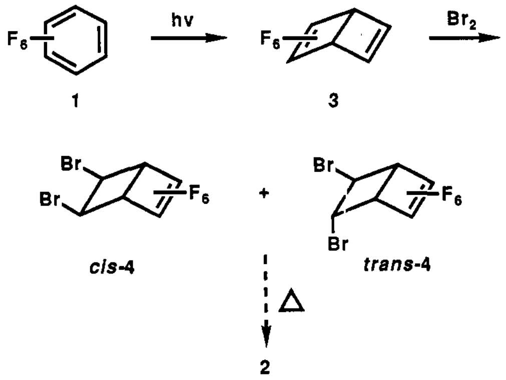


cis-**2**



trans-**2**

Scheme I



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).

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

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