

Hexafluorobenzene Photochemistry: Wellspring of Fluorocarbon Structures

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ABSTRACT

Ultraviolet irradiation of hexafluorobenzene in the vapor phase gives exclusively its Dewar valence isomer, from which a wealth of highly fluorinated compounds has been derived. Photoexcited in solution, hexafluorobenzene is capable of cycloaddition with a variety of unsaturated molecules. Like the Dewar benzene, resulting adducts have served as intermediates en route to many new fluorocarbons and fluorocarbon derivatives.

The synthetic photochemistry of hexafluorobenzene (**1**)



originated in 1966, when Haller¹ and Camaggi et al.² discovered its isomerization to the Dewar form (**2**) upon UV irradiation in the vapor phase. Both Camaggi's group³ and Haszeldine's group⁴ explored the chemistry of the Dewar benzene.⁵ Bryce-Smith et al.⁶ and later Zupan and Sket⁷ carried out photocycloadditions of **1** to unsaturated hydrocarbons, and Barlow and co-workers studied its photooxidation.⁸

Research in our laboratory involving hexafluorobenzene photochemistry began with most of the above work as background. Our contributions are conveniently divided into two categories: chemistry derived from the Dewar benzene, and chemistry based on photocycloadditions of the benzene. These investigations have been part of a program in our laboratory, the objective of which is a fuller understanding of fluorocarbon chemistry, i.e., of the consequences of complete substitution of fluorine for the hydrogen in organic molecules.

Syntheses from the Dewar Benzene

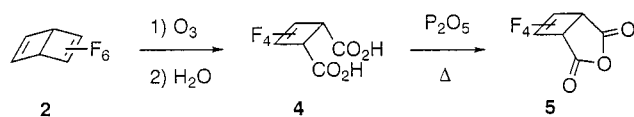
Photolysis of **1** at 254 nm gives in excellent yield a single valence isomer,⁹ the highly strained Dewar benzene **2**, which is a very reactive and versatile synthetic intermediate. It is formed only in the vapor phase, and when condensed it has a tendency to detonate capriciously. In our laboratory it is always pumped from the quartz flasks

in which it is prepared into a cold trap containing a solvent. We have handled 30% solutions of **2** for many years without incident.

Tetrafluorocyclobutadiene and Tetrafluorocyclopentadienone. Our work began with a quest for tetrafluorocyclobutadiene (**3**) at a time when the nature of the

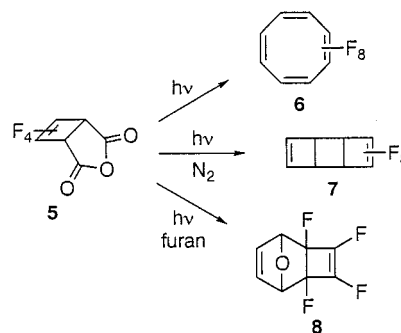


ground state of the parent hydrocarbon was a matter of vigorous debate. The plan was to ozonize hexafluoro Dewar benzene selectively and then to photolyze the monoozonide, generating the cyclobutadiene. Selectivity was no problem, but a normal ozonide was not formed. The desired oxidation state was achieved, however, as revealed by the fact that water transformed the ozonation product into diacid **4**. Vapor phase photolysis of the



derived anhydride (**5**) gave perfluorocyclooctatetraene (**6**), but if nitrogen (500 Torr) was present as a bath gas, the product was instead tricyclooctadiene **7** (Scheme 1).¹⁰

Scheme 1



When furan was present during the reaction, a Diels–Alder adduct (**8**) with **3** was formed, thus confirming the intermediacy of tetrafluorocyclobutadiene in the photolysis. These findings led us to surmise that **3**, generated by photoextrusion of CO and CO₂ from the anhydride, dimerized to give **7**. When nitrogen was present to provide collisional cooling for the vibrationally hot **7**, the molecule survived, but in its absence this very strained diene rattled itself apart to yield cyclooctatetraene **6**.

Further study of the photolysis undermined this tidy interpretation, for at short reaction times with nitrogen present the cyclooctatetraene was detected, and the ratio of **6** to **7** increased as time zero was approached!¹¹ Thus, it appeared that **6** was the precursor of **7** instead of the converse. Irradiation of **6** under the reaction conditions (254 nm) did indeed give **7**, and nitrogen was found to accelerate the photoisomerization dramatically. The anti and syn isomers of **7** were formed in the ratio 20:1. The role of nitrogen was probably to provide collisional

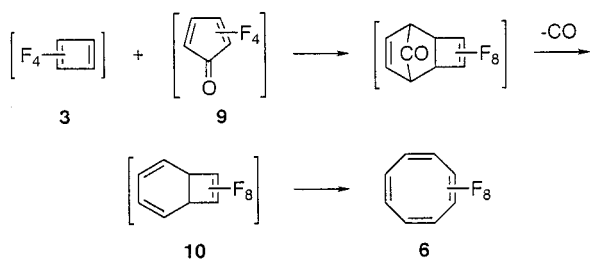
David M. Lemal received an A.B. degree from Amherst College and a Ph.D. from Harvard University with R. B. Woodward. After seven years on the faculty of the University of Wisconsin in Madison, he joined the Dartmouth Chemistry Department, where he is presently the Albert W. Smith Professor of Chemistry. His research interests are focused particularly on fluorocarbons and their derivatives, but also include stable carbenes, azulenes, and other organic species with unusual properties and chemistry.



deactivation for hot **7**, as originally supposed, but for **7** created via a different route.

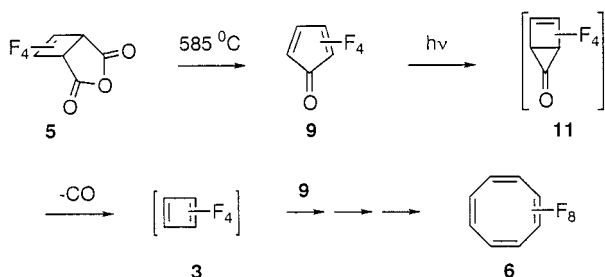
How could the cyclooctatetraene arise, if not from its tricyclic isomer? If in addition to **3**, photolysis of the anhydride gave tetrafluorocyclopentadienone (**9**), cross dimerization could answer the question. Maier has observed this kind of behavior in the matrix photolysis of other cyclobutenedicarboxylic anhydrides.¹² Loss of CO thermally or photochemically from the Diels–Alder adduct of **3** and **9** would give triene **10**, which opens spontaneously (as discussed later) to tetraene **6** (Scheme 2).¹³

Scheme 2

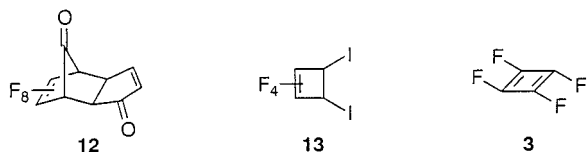


Support for this interpretation became available when we found that flash vacuum pyrolysis of anhydride **5** gave dienone **9**, and that vapor phase photolysis of this compound at low pressure yielded **6**.¹⁴ This result is understandable in terms of photoextrusion of CO from **9**, probably via **11**, followed by the cross dimerization proposed above (Scheme 3).

Scheme 3



The orange dienone **9**, which we have also prepared by flash vacuum pyrolysis of tetrafluoro-*o*-benzoquinone,¹⁵ dimerizes rapidly at room temperature as a liquid but has a half-life of many hours as a vapor at pressures below 1 Torr. Its Diels–Alder dimer **12**, which surprisingly

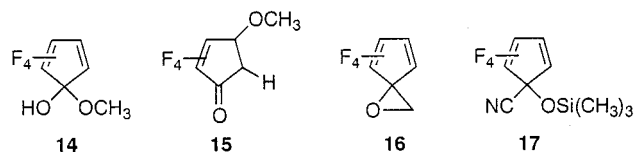


has the exo configuration, slowly loses the bridging CO

even at room temperature.¹⁴ Thus, loss of CO from the adduct of **3** and **9**, born vibrationally hot in the vapor phase, may not require the help of a photon.

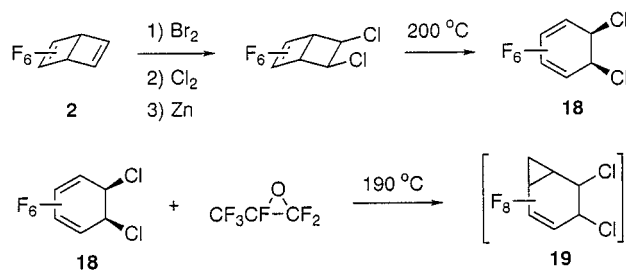
We have found that mercury-sensitized vapor-phase photolysis of tetrafluoro-3,4-diiodocyclobutene (**13**) in the presence of furan yields Diels–Alder adduct **8**, thus providing the first clear evidence that **13** can also function as a source of cyclobutadiene **3**.¹⁶ Very recently, Radziszewski and Petersson have been able to generate **3** in an argon matrix at ~ 10 K from both anhydride **5** and diiodide **13**, and to identify it by its infrared spectrum.¹⁷ The close agreement they obtained between the experimental spectrum and that calculated at the Becke3LYP/cc-pVDZ level of theory is convincing evidence for their structure assignment. Remarkably, the cyclobutadiene is a *nonplanar* singlet in its ground state. The C_{2h} structure, unprecedented for a cyclobutadiene lacking very bulky groups, has one pair of fluorines above the plane of the rectangular carbon framework and the other pair below. This geometry can be rationalized as the result of a conjunction of two factors, Bent's rule¹⁸ and antiaromaticity. Pyramidalization of the carbons serves both to increase the p character in the C–F bonds and to diminish the overlap in the 4π system.

In an effort to create a $(\text{CF})_4$ synthon for building valence isomers of higher perfluoroannulenes, the carbonyl group of dienone **9** was modified to inhibit dimerization. At low temperatures, methanol containing a trace of methoxide added to form hemiketal **14**, but as the

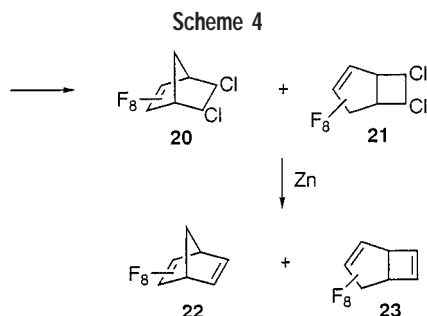


solution warmed to room temperature this kinetic product gave way to the thermodynamic adducts *cis*- and *trans*-**15**.¹⁹ Attempts to cap **14** with diazomethane led instead to spirooxirane **16**. Prepared at low temperatures, the cyanohydrin of **9** decomposed at 0 °C, but base-catalyzed addition of trimethylsilyl cyanide to the dienone gave a stable adduct (**17**) which dimerized only slowly at 100 °C. This compound may well serve as a $(\text{CF})_4$ synthon, as the potential carbonyl group can be unmasked and extruded from its cycloadducts.

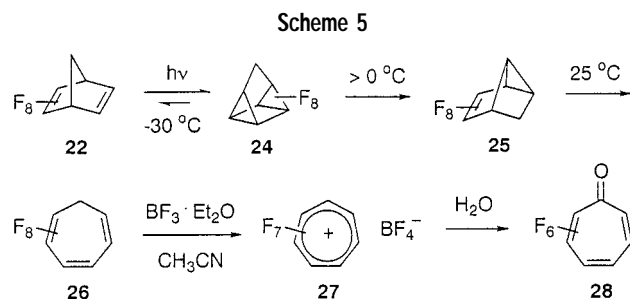
Perfluorotropylium Ion, Perfluorotropone, and Perfluorobarrelele. A synthon for hexafluorobenzene, dichlorocyclohexadiene **18**, was prepared in four steps (70%) from Dewar benzene **2**.²⁰ Protection of a double bond of



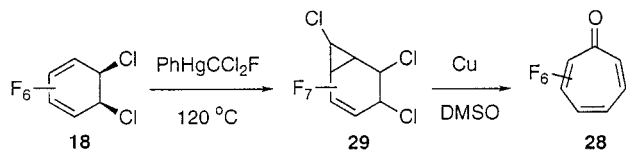
2 by bromine limits attack of chlorine to one double bond and enforces syn addition to the exo face of the molecule. The difluorocarbene adduct **19**, formed by treatment of **18** with hexafluoropropylene oxide at 160–190 °C, underwent vinyl cyclopropane rearrangement under the reaction conditions, giving **20** and **21** (Scheme 4).²¹



Dechlorination of these adducts yielded perfluorodienes **22** and **23**. The latter was welcomed as a potential precursor to the unknown perfluorotropylium ion, but in our hands did not serve as such. However, with the help of serendipity, norbornadiene **22** played that role. UV irradiation at –30 °C of **22** effected reversible isomerization to perfluoroquadricyclane (**24**), resulting in a steady state **24:22** ratio of ~60:40 (Scheme 5).²² Upon warming



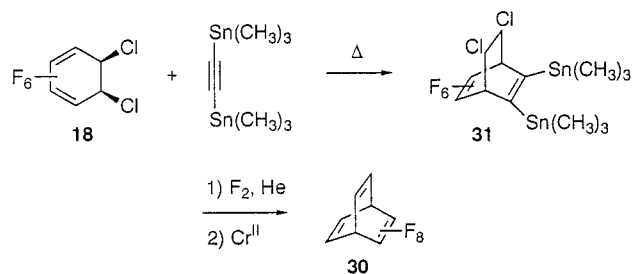
above 0 °C, **24** isomerized to tricycloheptane **25**, which at room temperature rearranged to perfluorotropilidene (**26**).²³ Brief treatment of **26** with boron trifluoride etherate yielded the desired perfluorotropylium tetrafluoroborate (**27**), which hydrolyzed with extreme ease to perfluorotroponone (**28**).^{23,24} The troponone was obtained more directly from the benzene synthon **18** by addition of chlorofluorocarbene generated from PhHgCCl₂F to give a stereoisomeric mixture of adducts (**29**) which was reduced with copper in DMSO.²⁵ Probably the perfluorotropylium ion



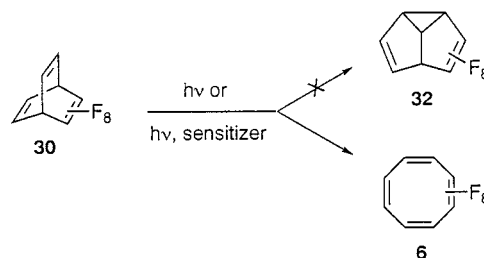
was formed and then attacked by the solvent to introduce the carbonyl oxygen.

Benzene synthon **18** also provided a route to perfluorobarrelene (**30**). Diels–Alder addition of **18** to bis(trimethylstannyl)acetylene yielded **31**, which upon fluorodestannylation and dechlorination gave the volatile, beautifully

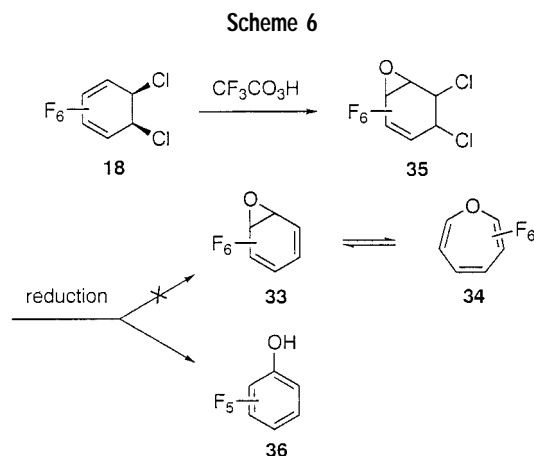
crystalline **30**.²⁶ We had hoped that photolysis of the



barrelene would yield perfluorosemibullvalene (**32**), in analogy to the parent hydrocarbon,²⁷ but both direct and sensitized photolysis just gave perfluorocyclooctatetraene (**6**).

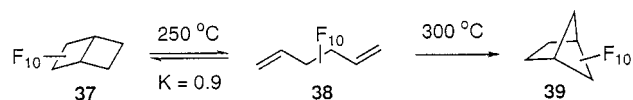


Epoxidation of **18** followed by dechlorination was intended to yield perfluorobenzene oxide (**33**) or its valence tautomer perfluorooxepin (**34**), but reduction of oxirane **35** with a variety of reagents gave only pentafluorophenol (**36**) (Scheme 6).²¹ A successful approach to the sensitive oxide is described later in this Account.



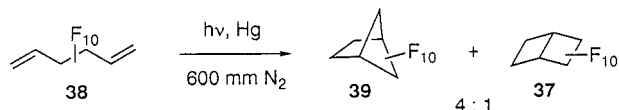
Interrelationships among C₆F₁₀ Valence Isomers.

Saturation of the double bonds of the Dewar benzene **2** with fluorine produced perfluorobicyclo[2.2.0]hexane (**37**).²⁸ At 250 °C, **37** exists in equilibrium with perfluoro-1,5-hexadiene (**38**),²⁹ with $K_{\text{eq}} = 0.9$. At higher temperatures



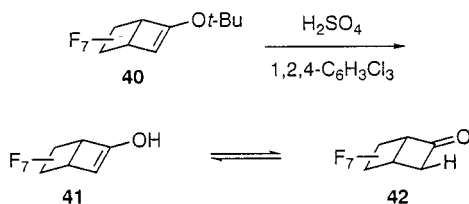
irreversible isomerization to the [2.1.1] isomer **39** becomes rapid. This situation contrasts sharply with that of the corresponding hydrocarbons, where the bicyclic isomers

rearrange to the diene upon heating.³⁰ The fact that at 250 °C the very strained **37** is slightly lower in free energy than diene **38** and **39** is distinctly more stable yet reflects the well-known driving force for highly fluorinated double bonds to become saturated.³¹ Mercury-sensitized vapor-phase photolysis of diene **38** also yields **39** and **37**, here in the ratio 4:1. The faster formation of **37** thermally but



39 photochemically from the diene can be understood by application of the Hammond postulate to the generation of intermediate biradicals.²⁸ Our results suggested that thermal and photochemical cyclization of perfluorodienes and -polyenes should be a fairly general route to bi- and perhaps polycyclic fluorocarbons; subsequent work has confirmed that surmise.^{32,33}

A Novel Keto–Enol System. Addition of fluorine across just one of the double bonds of Dewar benzene **2** followed by treatment with *tert*-butoxide gave enol ether **40**.^{34,35} Cleavage of **40** with sulfuric acid produced initially the enol **41**, which tautomerized readily to ketone **42**. We



found that 7% of the enol remained at equilibrium in carbon tetrachloride, however, and in mildly Lewis basic solvents such as acetonitrile and ether *only enol* could be detected. The dramatic shift in equilibrium in Lewis basic media is a consequence of the powerful hydrogen-bond donor ability of the perfluoroenol. The remarkable stability of this enol relative to its ketone, as compared with hydrocarbon-derived enols, led us into an extensive investigation of highly fluorinated keto–enol systems. Enols **43**³⁵ and **44**³⁶ were found to be much more stable



than their ketones even in carbon tetrachloride; they are the most stable unhindered, unconjugated enols known to date.

Acyclic perfluoroenols were found to be far less stable relative to their ketones,^{37,38} a result which has led with the help of quantum mechanical calculations to the recognition of a previously unnoticed phenomenon: strong steric interactions in internal acyclic perfluoroalkenes in general.³⁹

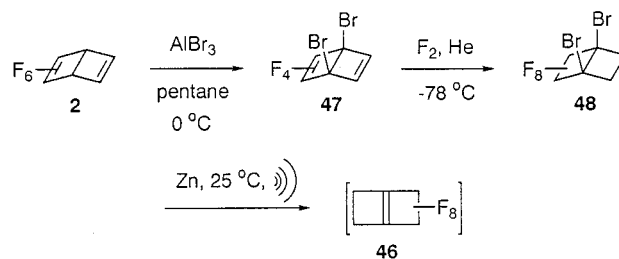
A Greatly Strained Perfluoroalkene. Wiberg's interesting work on the highly reactive bicyclo[2.2.0]hex-1(4)-ene

(**45**)⁴⁰ stimulated us to attempt the synthesis of its per-

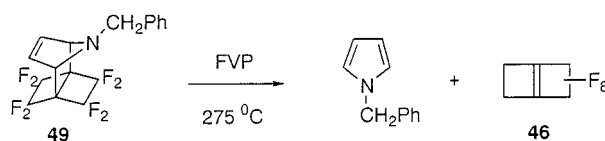


fluoro counterpart, **46**. Treatment of Dewar benzene **2** with aluminum bromide replaced the bridgehead fluorines selectively,⁴¹ and fluorination of the resulting dibromide **47** yielded a promising precursor (**48**) for the desired alkene (Scheme 7).⁴² Zinc transformed **48** into **46** at room

Scheme 7



temperature, as revealed by trapping with dienes in Diels–Alder reactions.⁴² The adduct with *N*-benzylpyrrole (**49**) underwent retro-Diels–Alder reaction upon flash vacuum pyrolysis at 275 °C, giving alkene **46** cleanly in high yield.⁴³



In contrast to the parent hydrocarbon, which dimerizes and polymerizes readily below 0 °C, **46** is a very stable liquid, albeit highly reactive.

Hydrocarbon **45** has been shown to have a planar skeleton, but it was not a foregone conclusion that **46** would “follow suit”. The combination of severe bond angle compression at the bridgeheads and electron withdrawal by the four CF₂ groups might suffice to induce pyramidalization at those carbon atoms (Figure 1).¹⁸ On the other



FIGURE 1. Likely geometries for alkene **46**.

hand, recent calculations by Wiberg have shown that fluorine substitution can have a planarizing influence on a small bicyclic alkene whose hydrocarbon parent is bent.⁴⁴ The absence of infrared absorption where the Raman spectrum reveals C=C stretching supports the centrosymmetric *D*_{2h} structure,⁴⁵ as do calculations at the HF/6-31G* and B3LYP/6-31G* levels of theory.⁴⁶ A recent electron diffraction study of the molecule by Hedberg et al. is in accord with these findings.⁴⁷

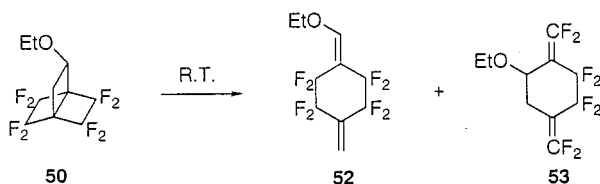
In addition to Diels–Alder reactions, the alkene has been shown to undergo [2 + 2] cycloadditions, 1,3-dipolar cycloadditions, ene reactions, attack by nucleophiles, addition of bromine and hydrogen, and electrocyclic ring

opening.^{42,43} When **46** is trapped with ethyl vinyl ether, a [2.2.2]propellane (**50**) is formed. Only one other repre-

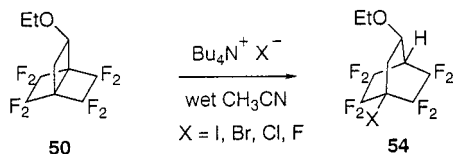


sentative of this highly strained ring system has been isolated, the carboxamido derivative **51** synthesized by Eaton and Temme.⁴⁸

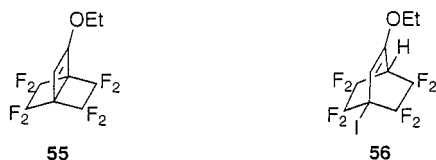
Propellane **51** spontaneously ring opened to bis-(methylene)cyclohexanes with a half-life of only ~28 min at 25 °C. Fortunately, the half-life for opening of **50** to give **52** and **53** was roughly 20 h at room temperature.⁴²



Whereas **51** added bromine across the central bond instantly at -70 °C, **50** failed to react with electrophiles at room temperature—even concentrated sulfuric acid in acetonitrile. The extremely strained central bond is easily cleaved by radicals and nucleophiles, however. Halide ions break that bond with clean regioselectivity, forming hydrogen halide adducts **54** in moist acetonitrile.⁴⁹



Alkene **46** has recently been trapped with ethoxyacetylene at low temperatures to give the first [2.2.2]-propellene (**55**),⁴³ which polymerizes rapidly upon warm-

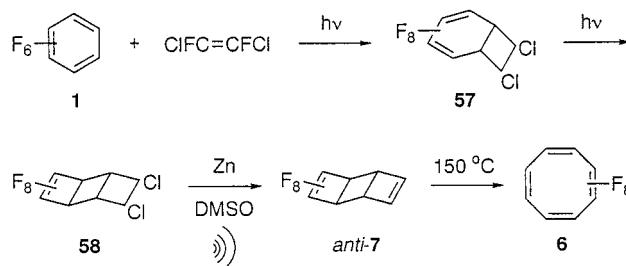


ing to room temperature. Treatment of the propellene in the cold with tetrabutylammonium iodide in moist acetonitrile yields the HI adduct **56**. Cleavage of a C-C bond in S_N2 fashion under such mild conditions is certainly a rare event in organic chemistry.⁵⁰

Syntheses Based on Photocycloaddition to Alkenes

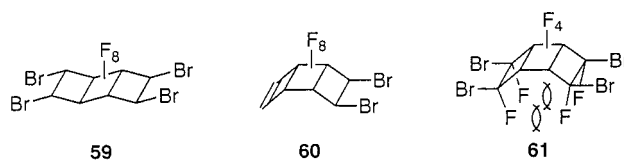
Octafluorocyclooctatetraene and Some of Its Valence Isomers. Photocycloaddition of hexafluorobenzene to 1,2-dichlorodifluoroethylene opens a more efficient route to octafluorocyclooctatetraene (**6**) (Scheme 8),⁵¹ first synthe-

Scheme 8



sized from anhydride **5** and cyclopentadienone **8** as described above. The initially formed [2 + 2] adducts (**57**) photocyclize under the reaction conditions to give a stereoisomeric mixture of *anti*-tricyclo[4.2.0]octenes (**58**). With assistance from ultrasound, zinc dechlorinates **58** to give *anti*-tricyclooctadiene **7** as volatile crystals which ring open cleanly to the tetraene **6** at 150 °C.

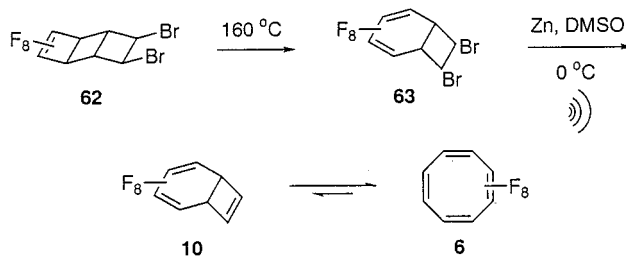
As noted earlier, photosensitized isomerization of **6** yields *anti*-7 accompanied by a small amount of *syn*-7. The two isomers are easily distinguished by their behavior toward bromine.⁵² In each case, addition of the halogen occurs exclusively in *exo*, *cis* fashion for steric reasons; the difference is that even at -20 °C the *anti* isomer starts to add a second equivalent of bromine to give **59** before



reaction of the first is complete, whereas the *syn* stops abruptly after a single equivalent has added at room temperature. Dibromide **60** eschews further bromination because of the severe crowding which tetrabromide **61** would experience in the *endo* cavity of the molecule.

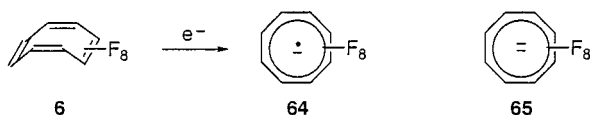
Anti dibromide **62** ring-opened at 160 °C, yielding an 87:13 mixture of *exo*, *cis* and *endo*, *cis* dibromodienes **63**.⁵³ Debromination of **63** at 0 °C and 0.05 Torr gave the extremely labile octafluorobicyclo[4.2.0]octa-2,4,7-triene (**10**), intercepted in a cold trap (Scheme 9). At 0 °C **10**

Scheme 9



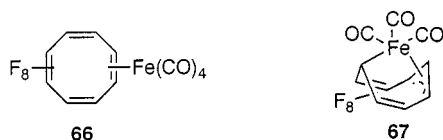
reverted to cyclooctatetraene **6** with a half-life of 14 min ($E_a = 18.9 \pm 0.6$ kcal/mol, $A = 1.1 \times 10^{12}$). Surprisingly, these values are indistinguishable from those for the parent hydrocarbon.⁵⁴ The amount of **10** in equilibrium with **6** at 20 °C was found to be 0.2(8)%,⁵⁵ as compared with 0.01% for the hydrocarbon parent of **10** at 100 °C.⁵⁶

Gamma irradiation at 77 K of cyclooctatetraene **6** in a 2-methyltetrahydrofuran glass by Williams et al. generated the radical anion **64**, which gave upon warming to 145 K



an isotropic ESR spectrum comprising nine lines with binomial intensity distribution.⁵⁷ The equivalence of the eight fluorines suggests a planar D_{8h} structure, and the ^{19}F hyperfine coupling constant of 10.92 G reveals that **64** is a π radical ion. This ESR spectrum resembles those of perfluoro benzenoid aromatic radical cations, a reasonable finding since both types of π system have one less than $4N + 2$ electrons. Note that the ^{19}F hyperfine coupling constant in the ESR spectrum of the perfluorobenzene radical anion is far larger (137 G) because the odd electron occupies a σ^* orbital in this case.⁵⁸ Attempts to generate the dianion **65** both chemically and cyclic voltammetrically indicated that it is an extremely unstable species.⁵⁹

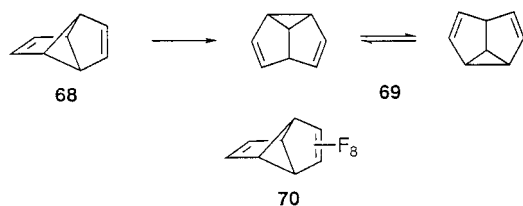
Cyclooctatetraene **6** has proven to be a versatile ligand in organotransition metal chemistry. Diiron nonacarbonyl in hexane at room temperature gave tetracarbonyl complex **66**, which at reflux was transformed into the oxidative



addition product **67**.⁶⁰ Cyclooctatetraene itself does not form an iron complex analogous to either. The Hughes group has since synthesized a large array of transition metal complexes of **6** spanning a remarkable range of structural types.⁶¹

Hexafluorobenzene photochemistry has also made available a variety of substituted perfluorocyclooctatetraenes and -bicyclooctatrienes,⁶² but space limitations preclude discussion of them here.

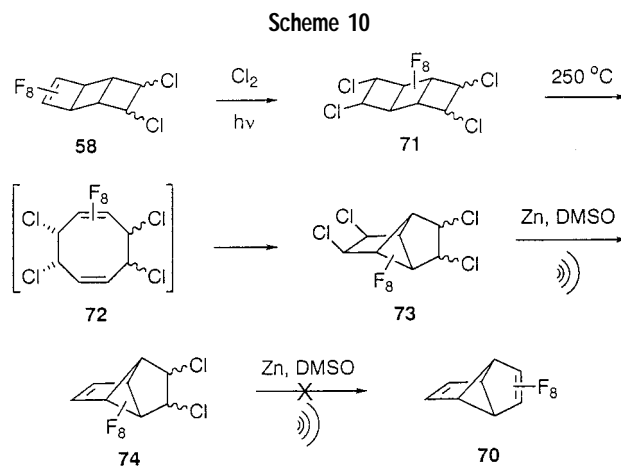
An Approach to Perfluorosemibullvalene. This molecule is a tempting target for synthesis in light of fluorine's penchant for destabilizing cyclopropane rings.⁶³ Weakening of the doubly allylic cyclopropane bond may result in an unusually low barrier for degenerate Cope rearrangement, and the barrier for the parent hydrocarbon (**69**) is



a mere 5.2 kcal/mol.⁶⁴ As noted above, perfluorobarrelene (**30**), unlike barrelene itself, failed to yield the semibullvalene (**32**) upon photolysis. Thus, a different synthetic

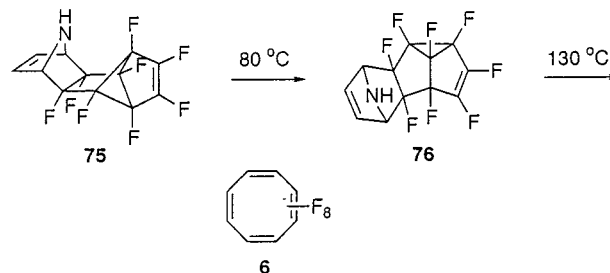
approach to **32** was mounted, based on the room temperature rearrangement of tricyclooctadiene **68** to semibullvalene.⁶⁵ With the expectation that the fluorocarbon counterpart of **68**, fluorodiene **70**, will behave analogously, **70** became the immediate synthetic objective.

Photochlorination of the stereoisomeric photoadducts **58** gave tetrachlorides **71**, which rearranged at 250 °C via cyclooctadienes **72** to the more stable tricyclic isomers **73** (Scheme 10).⁶⁶ Compounds **73** were reduced with zinc to



dichlorides **74**, but all attempts to reductively eliminate the second pair of chlorines led to complete destruction. Dichlorides **74** underwent Diels–Alder reactions and [2 + 2] cycloaddition with a triazolinedione, and the resulting adducts were successfully dechlorinated. Therefore, the problem lay in having both double bonds present in the twisted tricyclic skeleton. The apparent lability of **70** makes sense by analogy to the parent hydrocarbon **68**, in which the double bonds interact with one another so effectively via the Walsh orbitals of the central cyclobutane ring that the compound displays substantial UV absorption even beyond 300 nm (where $\epsilon = \sim 190$).⁶⁷ The interaction both lowers the LUMO and raises the HOMO, resulting in high reactivity.⁶⁸

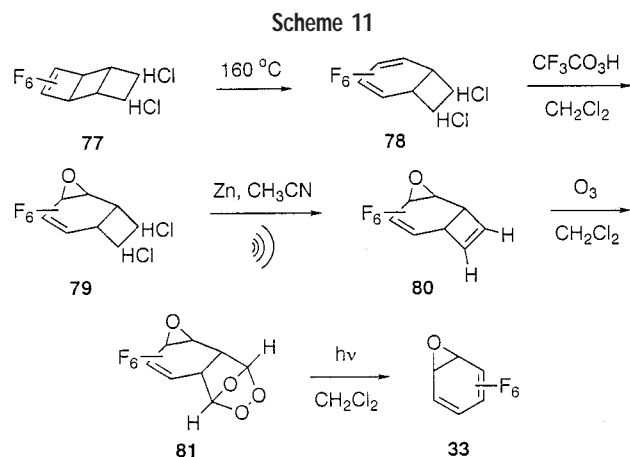
Dechlorination of the Diels–Alder adduct from dichloride **74** and pyrrole yielded **75**, which rearranged at



80 °C to **76**. Since this pentacyclic diene is formally the Diels–Alder adduct of perfluorosemibullvalene (**32**) with pyrrole, it was hoped that thermolysis at a higher temperature would bring about retro-Diels–Alder reaction and yield the elusive target molecule. The reaction was carried out at 130 °C under reduced pressure to remove **32** as it was formed, but the fluorocarbon that distilled

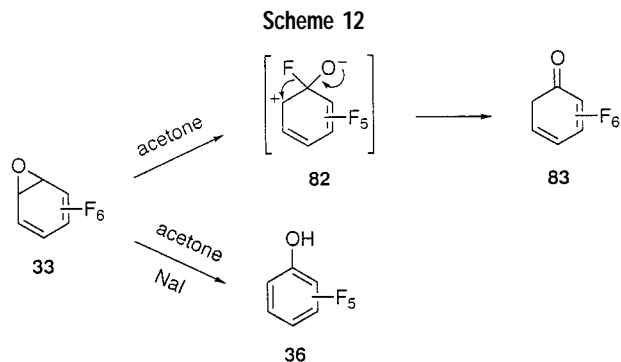
was cyclooctatetraene **6**.⁶⁶ A gentler final step will be required to obtain the fragile semibullvalene.

Hexafluorobenzene Oxide and Hexafluorooxepin. The parent benzene oxide and oxepin are a rapidly equilibrating pair of valence isomers with interesting spectroscopic properties and reactivity.⁶⁹ Unsuccessful attempts to prepare their perfluoro counterparts in England^{8b} and in our laboratory²¹ made it clear that these compounds are very sensitive. For that reason, a synthetic plan was developed which culminated in a photochemical step that could be performed in an inert solvent at low temperatures, if necessary (Scheme 11). The stereoisomeric mix-



ture of photoadducts **77** obtained from hexafluorobenzene and 1,2-dichloroethene was separated by distillation into *cis* and *trans* fractions, which were thermally ring opened to *endo,cis*-**78** and *trans*-**78**, respectively. Treatment with peroxytrifluoroacetic acid transformed these dienes into epoxides (**79**), ultrasound-assisted dechlorination of which with zinc gave in low yield the delicate diene **80**. Ozonation of this diene yielded an *exo/endo* mixture of ozonides (**81**). The product of photolysis of the ozonides in Pyrex was fairly complex, but it contained a single volatile compound: hexafluorobenzene oxide (**33**).⁷⁰

Though quite stable at room temperature in typical nonpolar solvents, **33** rearranges cleanly to hexafluorocyclohexa-2,4-dienone (**83**) when the solutions are warmed. It also does so in acetonitrile or acetone even in the cold, presumably via zwitterion **82** (Scheme 12). The oxide is



cleanly reduced under very mild conditions (e.g., sodium iodide in acetone at room temperature) to pentafluoro-

phenol (**36**), thus explaining our earlier failure to obtain it by reduction of dichlorooxirane **35**.²¹

While the ¹⁹F NMR spectrum of **33** at -40 °C comprises three resonances with well-resolved spin-spin splitting, all three broaden and then narrow again as the temperature is raised. This behavior reveals a dynamic equilibrium with an isomer, undoubtedly the oxepin (**34**). The



temperatures where line widths are maximal are different for each signal, and correlate nicely with the magnitude of estimated chemical shift differences between benzene oxide fluorines and their oxepin counterparts. The oxepin was not detected directly, however, and it is clear that the valence isomer equilibrium favors benzene oxide **33** very heavily.⁴⁶ In contrast, the parent benzene oxide-oxepin equilibrium is quite evenly balanced.⁶⁹ At the HF/6-31G*//6-31G* level of theory, the benzene oxide **33** is indeed more stable than oxepin **34** ($\Delta G = -2.17$ kcal/mol, 25 °C⁷¹), but at lower levels (e.g., HF/3-21G//3-21G) the opposite is true. With the destabilization of three-membered rings by fluorine in mind,⁶³ we had anticipated at the outset that the **33**-**34** equilibrium would lie far on the side of **34**. Surprises such as this one remind us of how much more there is to learn about organofluorine chemistry.

Conclusions

The chemistry described in this Account illustrates several of the fundamental differences that distinguish fluorocarbons and their derivatives from their hydrocarbon counterparts. Fluorine's great electronegativity manifests itself in multiple ways: in the tendency for fluorinated double bonds to become saturated (perfluorodiene cyclizations such as the **38**-**37**, **38**-**39**, and **72**-**73** transformations); in the destabilization of cyclopropanes (spontaneous rearrangement of perfluoroquadracyclane (**24**) to perfluorotropilidene (**26**)); in the stabilization of cyclobutane rings (robustness of perfluorobicyclo[2.2.0]hex-1(4)ene (**46**) and [2.2.2]propellane **50**); in the distortion of perfluorocyclobutadiene (**3**) from planarity; in the destabilization of perfluoroketones (as revealed by the relative stability of enols such as **41**, **43**, and **44**); and in the resistance of propellane **50** to electrophilic attack together with its susceptibility to nucleophilic attack). Steric effects resulting from the fact that fluorine's van der Waals radius is about 20% larger than that of hydrogen and its bond to carbon about 20% longer than the C-H bond are also apparent in the chemistry described above. Examples include the dramatic shifts in keto-enol equilibria from cyclic to acyclic systems and the failure of tricyclic dibromide **60** to brominate further. The great resistance of strained alkene **46** to dimerization and polymerization, as compared with the parent hydrocarbon, is almost certainly steric as well as electronic in origin.

Since hexafluorobenzene (**1**) is relatively inexpensive for a fluorocarbon and highly reactive when irradiated with UV light, its photochemistry provides an excellent start for synthetic pathways, leading to a great variety of fluorinated compounds. Laboratory syntheses based on Dewar benzene **2** are limited in scale by practical considerations, viz., its dangerous nature and the fact that it can be made only in the vapor phase. On the upside, it follows that the diverse solution photochemistry of **1** is not complicated by competing valence isomerization, and its photoreactions in solution can be carried out on a large scale. This Account has described the preparation of a hearty smorgasbord of organofluorine compounds originating from hexafluorobenzene photochemistry, and the prospects are bright for creating many new delicacies from this source in the future.

As an example, the chemistry of annulenes and their valence isomers has been a remarkably rich source of interesting phenomena,⁷² but the chemistry of their perfluoro analogues is in its infancy. We have synthesized just 5 of the 20 theoretically possible (CF)₈ isomers (all from hexafluorobenzene), and not a single (CF)₁₀ or higher annulene isomer is known.^{73,74} Hexafluorobenzene photochemistry can be expected to play a key role in the development of this area of fluorocarbon research.

I am deeply indebted to the many able and dedicated co-workers—undergraduate, graduate and postdoctoral—whose accomplishments are briefly outlined in this Account, and to many others whose work is not described owing to space limitations. We have enjoyed generous financial support from the National Science Foundation, the Air Force Office of Scientific Research and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

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