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D. M. Lemal

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The objective of this project was to synthesize and study the chemistry of an array of fluorocarbons and fluorocarbon derivatives in order to further understanding of fluorine as substituent in organic chemistry. Target molecules, all of which incorporated conjugation and/or strain, were chosen on the basis of unusual and/or interesting structural features. This investigation has accomplished the synthesis of many new fluorocarbons and derived molecules, and has included exploration of new synthetic methodology in fluorocarbon chemistry, determination of thermodynamic and kinetic parameters for fluorocarbon valence isomerizations, study of negative hyperconjugation, and examination of mechanisms of fluorocarbon reactions. Much has been learned about how to synthesize perfluorinated annulenes and their relatives, and much information has been acquired about potential energy surfaces for fluorocarbon valence isomerizations. A study of rotational barriers in alpha-fluoramines has revealed that negative hyperconjugation can have powerful energetic consequences even in neutral molecules. Insights into fluorocarbon reaction mechanisms, both thermal and photochemical, have emerged from synthetic explorations as well as from explicitly mechanistic studies.

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## COMPLETED PROJECT SUMMARY

1. TITLE: Synthesis and Chemistry of Strained and Conjugated Fluorocarbons

1. PRINCIPAL INVESTIGATOR: David M. Lemal  
Department of Chemistry  
Dartmouth College  
Hanover, NH 03755

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4. GRANT NUMBER: AFOSR-86-0130

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6. SENIOR RESEARCH PERSONNEL: Rahman, M.M.

7. JUNIOR RESEARCH PERSONNEL: Correa, R.A.      Goldman, G.D.  
Jensen, B.A.      Kendall, J.T.  
McCoy, C.H.      Morgan, K.M.  
Roberts, B.E.      Salsvier, C.H.  
Spector, T.      Takenaka, N.E.

8. PUBLICATIONS: Rahman, M.M.; Lemal, D.M.; Dailey, W.P. "Negative Hyperconjugation. The Rotation-Inversion Barrier in alpha-Fluoramines", *J. Am. Chem. Soc.* 1988, 110, 1964-6.

Dailey, W.P.; Correa, R.A.; Harrison, E., III; Lemal, D.M. "The 5,6-Dichlorohexafluorocyclohexa-1,3-dienes: Hexafluorobenzene Synthons", *J. Org. Chem.*, in press.

Soelch, R.R.; McNierney, E.; Tannenbaum, G.A.; Lemal, D.M.; "The Synthesis and Chemistry of Highly Fluorinated Bicyclo[2.2.0]hexenones", *J. Org. Chem.*, in press.

Dailey, W.P.; Ralli, P.; Wasserman, D.; Lemal, D.M. "Cycloadditions of cis-5,6-Dichlorohexafluorocyclohexa-1,3-diene", *J. Org. Chem.*, in press.

Spector, T.; Rahman, M.M.; Shafer, P.R.; Lemal, D.M. "Bond-Shift Isomerization of Heptafluorocyclooctatetraene", *J. Am. Chem. Soc.*, submitted for publication.

### 9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective of this project was to synthesize and study the chemistry of an array of fluorocarbons and fluorocarbon derivatives in order to further understanding of fluorine as substituent in organic chemistry. Target molecules, all of which incorporated conjugation and/or strain, were chosen on the basis of unusual and/or interesting structural features. This investigation has accomplished the synthesis of many new fluorocarbons and derived molecules, and has included exploration of new synthetic methodology in fluorocarbon chemistry, determination of thermodynamic and kinetic parameters for fluorocarbon valence isomerizations, study of negative hyperconjugation, and examination of mechanisms of fluorocarbon reactions. Much has been learned about how to synthesize perfluorinated annulenes and their relatives, and



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**for**  
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Institution: Dartmouth College, Hanover, N. H. 03755

Principal Investigator: David M. Lemal

## Summary of Accomplishments

Investigations carried out with the support of AFOSR-86-0130 have included synthesis of many new fluorocarbons and fluorocarbon derivatives, exploration of new synthetic methodology in fluorocarbon chemistry, determination of thermodynamic and kinetic parameters for fluorocarbon valence isomerizations, study of negative hyperconjugation, and examination of mechanisms of fluorocarbon reactions. Through failures as well as successes we have learned a great deal about how to synthesize perfluorinated annulenes and their relatives. We have acquired much information about potential energy surfaces for fluorocarbon valence isomerizations, information which through comparison with data on the corresponding hydrocarbon systems enriches our knowledge and understanding of fluorine substituents effects on molecular properties and chemical reactivity. Our study of rotational barriers in alpha-fluoramines has revealed that negative hyperconjugation can have powerful energetic consequences even in neutral molecules. Insights into fluorocarbon reaction mechanisms, both thermal and photochemical, have emerged from our synthetic explorations as well as from explicitly mechanistic studies

Lessons learned in the work described here set the stage for synthesis of novel, yet-unknown fluorocarbons and for physical organic investigations of their nature and chemistry. In the interest of conciseness, the summary presented below of our work under AFOSR-86-0130 does not include all of the projects investigated. This account is organized under three headings: Synthetic Methodology and its Applications, Negative Hyperconjugation, and Other Valence Isomerizations.

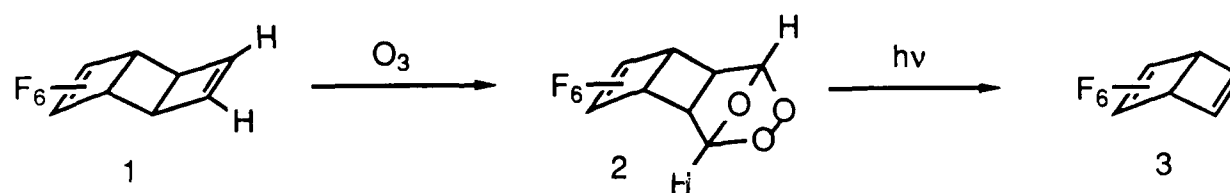
### Synthetic Methodology and its Applications

*Protection of fluorinated double bonds.* This is a central problem for us in the synthesis of perfluorinated annulenes and their valence isomers. Protection by bromination or chlorination is useful but limited, in the former case because the bromofluorocarbons decompose at elevated temperatures and in the latter because deprotection may require conditions too vigorous for a delicate fluorocarbon product to survive. In certain instances base-induced elimination of HCl would enjoy an advantage over reductive dehalogenation, but we discovered in exploring this option that HF elimination competes effectively against HCl elimination if the stereochemistry is not optimal. Vicinal dechlorination and debromination do have the virtue of working even when the geometry for concerted elimination is poor.

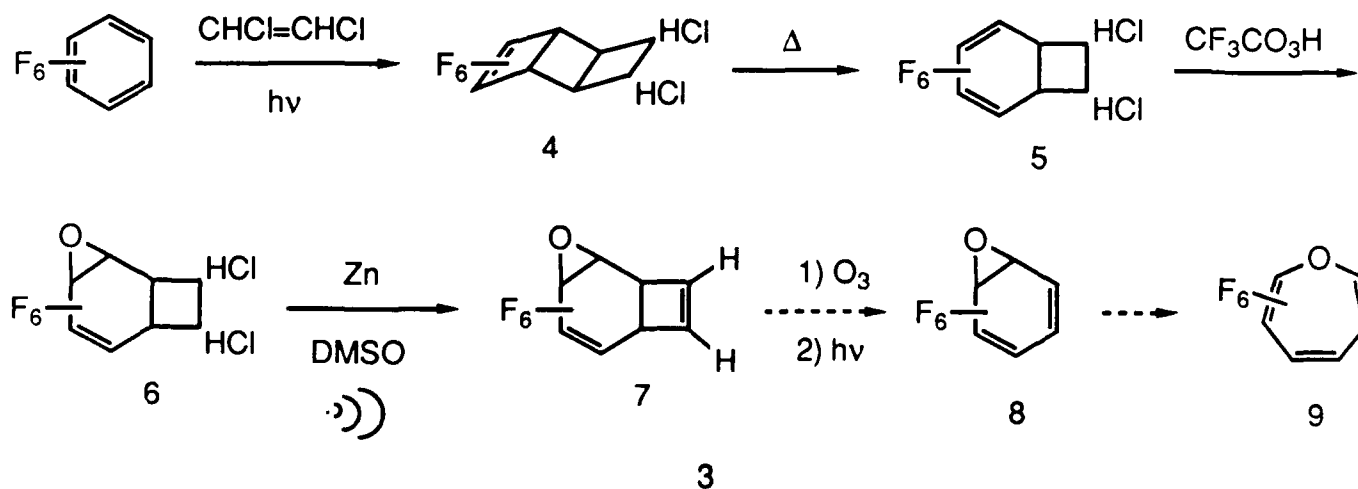
Thus, much effort has been devoted to developing alternative strategies for double bond protection, as described in the Second Interim Report. It is highly desirable that the final deprotection step be photochemical in nature in order that very labile fluorocarbons can be generated and studied at low temperatures. Cycloaddition of 2-chlorodiazaoethane was envisioned, followed at the appropriate stage of the synthesis by elaboration of a 2,3-diazacyclopentenone ring and photoelimination of nitrogen and carbon monoxide to regenerate the double bond. This scheme was

eventually abandoned, in part because of the danger in handling the capriciously explosive diazo compound. Efforts to synthesize 4-substituted triazolinediones capable of forming easily degradable cycloadducts with fluoroolefins were frustrated by the previously unknown and quite surprising tendency of the parent triazolinedione to acylate and alkylate at the 1- rather than the 4-position.

We therefore chose the unusual strategy of protecting double bonds with an etheno bridge, then eliminating the bridge via photolysis of the derived ozonide. This plan worked very well on the model compound **1**. Ozone reacted selectively with the relatively electron-rich unsubstituted double bond, and photolysis (either direct or sensitized) of the resulting ozonide **2** yielded hexafluorodewarbenzene (**3**), together with some hexafluorobenzene.

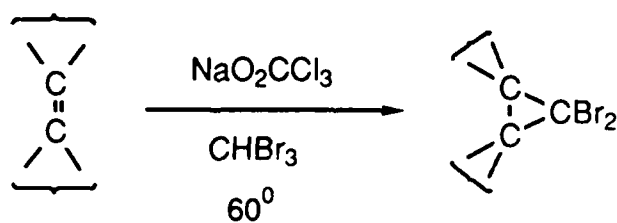


*Applications of the etheno bridge strategy.* Thus encouraged, we designed a synthesis of the elusive hexafluorobenzene oxide (**8**) based on this idea. Previous abortive attempts to prepare this compound in our laboratory and in England had suggested that it is very sensitive. Cycloadduct **4**, first prepared under our previous AFOSR grant, was thermally ring opened to **5**, epoxidized with peroxytrifluoroacetic acid to give **6**, then reductively dechlorinated with the assistance of ultrasound. The dechlorination step needs considerable refinement, but we are at last working on the crucial ozonation/photolysis sequence on diene **7**. The expected benzene oxide **4** will undoubtedly ring open to hexafluorooxepin **9** under mild conditions; we look forward to exploring the chemistry of both **8** and **9**.



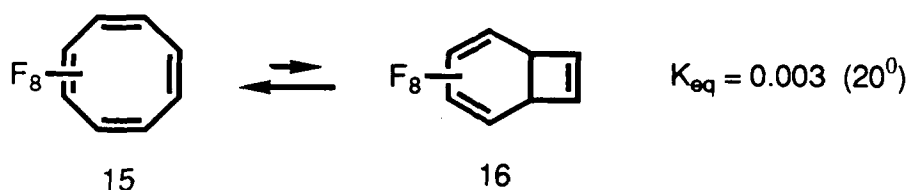


separated. We have been able to cyclopropanate vinylidene bromide, with which the Makosza method fails completely, using the new method.

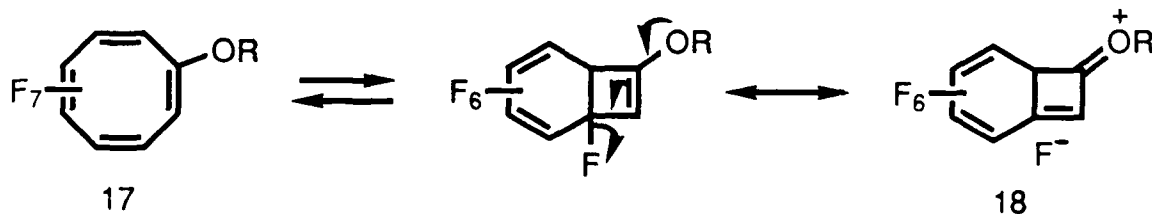


### Negative Hyperconjugation

*Alkoxyperfluorocyclooctatetraenes.* Octafluorocyclooctatetraene (**15**) exists in equilibrium at room temperature with a mere trace of its bicyclo[4.2.0]octa-2,4-triene valence isomer (**16**). We

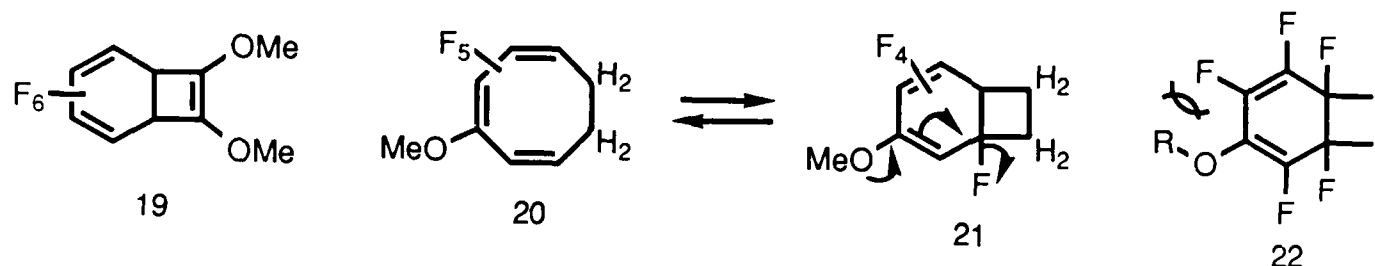


were thus very surprised to find that isopropoxyperfluorocyclooctatetraene (**17**, R=i-Pr) has an equilibrium constant  $>1$  for the corresponding valence isomerization, and that it gives only one of the four possible bicyclic isomers. The methoxy analog is very similar, but as the R group in **17** becomes electron withdrawing  $K_{eq}$  drops precipitously. This is obvious with R=CH<sub>2</sub>CF<sub>3</sub>, and with R=CH(CF<sub>3</sub>)<sub>2</sub> it is easy to miss detecting the bicyclic form. A possible explanation for this remarkable dependence of the equilibrium constant, apparently on the electron donor ability of the oxygen, is stabilization of the bicyclic form by negative hyperconjugation involving one of the



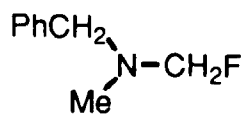
bridgehead fluorines (**18**). Indeed, when two adjacent methoxy groups were present so that both bridgehead fluorines could become involved in negative hyperconjugation, the compound existed essentially entirely in the bicyclic form **19**. Negative hyperconjugation was also possible in other

bicyclic isomers having the alkoxy substituent(s) on the six-membered ring, yet the only bicyclic forms observed were **18** and **19**. Cyclooctatriene **20**, which can form only one bicyclic form (**21**), was synthesized and its equilibrium constant for cyclization was compared with that of the analog lacking the methoxy group.  $K_{eq}$  for **20** was larger by a factor of only about four, indicating that negative hyperconjugation in **21** is of little importance. For efficient negative hyperconjugation the alkoxy substituent must lie approximately in the ring plane; on the 4-membered ring this poses no problem, but steric repulsion when the group is located on the 6-ring (see **22**) may inhibit the

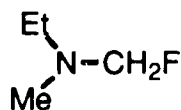


interaction. Further experiments will be required to evaluate convincingly the role of negative hyperconjugation in determining equilibrium constants for valence isomerization of alkoxyperfluorocyclooctatetraenes.

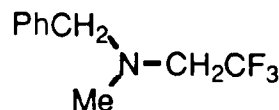
*alpha-Fluoramines.* Our experience with the alkoxy compounds above stimulated us to examine negative hyperconjugation in *alpha*-fluoramines, where the donor atom is excellent, in order to see how large the effect can be in a neutral molecule. We synthesized **23** and **24** and determined their C-N rotation-inversion barriers by dynamic NMR. For single bonds connecting small groups the free energy barriers were strikingly high: 10.1-10.2 kcal/mole. That these were not simply inversion barriers was confirmed by our finding that the pure inversion barrier in model compound **25** was considerably smaller. Here the  $CF_3$  group mimics the inductive effect of the F in **23** but does not match its ability to hyperconjugate. Pople's Fourier analysis of the *ab initio*-calculated barrier for *alpha*-fluoromethylamine indicates that half the barrier height is attributable to negative hyperconjugation and the balance to dipole-dipole repulsion and torsional strain. On this basis, we conclude that negative hyperconjugation accounts for ~5 kcal/mole of the barriers we found experimentally.



**23**



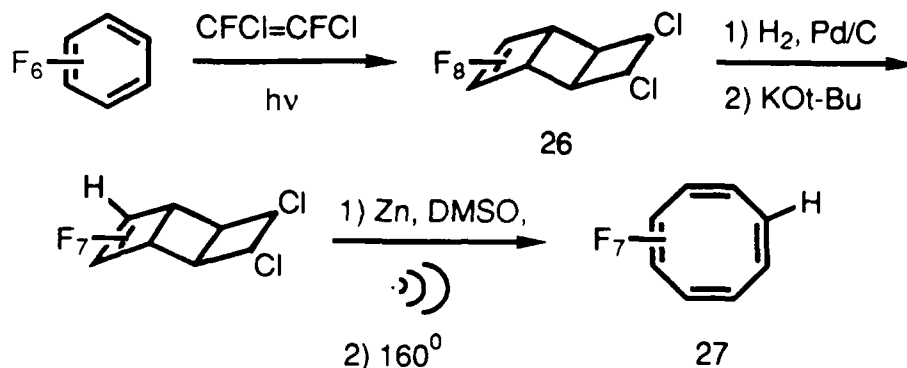
**24**



**25**

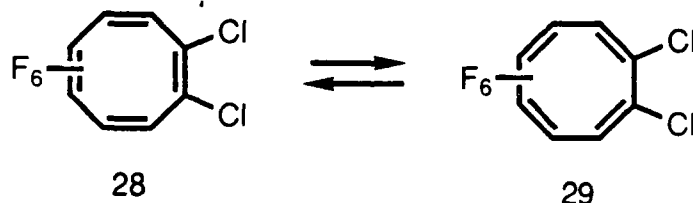
## Other Valence Isomerizations

*Thermal.* Heptafluorocyclooctatetraene (**27**) was synthesized from hexafluorobenzene via photoadduct **26**. The bond-shift barrier was determined for this simple derivative of

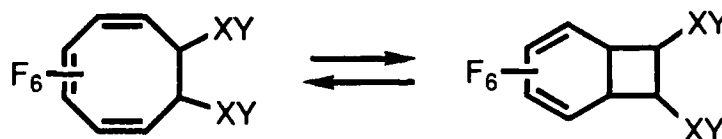


perfluorocyclooctatetraene by  $^{19}\text{F}$  NMR spin-saturation transfer experiments carried out at elevated temperatures. We found an activation enthalpy of  $21.1 \pm 0.9$  and an activation entropy of  $-10.2 \pm 2.5$  eu. The former value is twice that for cyclooctatetraene itself, probably because of nonbonded repulsions in the transition state. In contrast, the rather large negative entropy of activation is very close to that found for the parent hydrocarbon. Carpenter has interpreted that observation as evidence for *heavy-atom tunneling*, which may well be occurring also in the fluorinated tetraene.

1,2-Dichloroperfluorocyclooctatetraene (**28**) was synthesized and found to have a free energy barrier to bond-shift isomerization of  $>30$  kcal/mole. Thus, this molecule and its slightly lower energy 1,8-isomer **29** are perfectly stable at ordinary temperatures, testimony again that steric interactions in the bond-shift isomerization transition state are much greater for the fluorocarbons than for their hydrocarbon counterparts.



A series of highly fluorinated cyclooctatriene/bicyclooctadiene systems, **30-32**, have been synthesized by methods similar to those for **27** and their electrocyclization equilibria have been studied. This investigation has revealed that complete substitution of fluorine for hydrogen on the



**30** X = Y = H

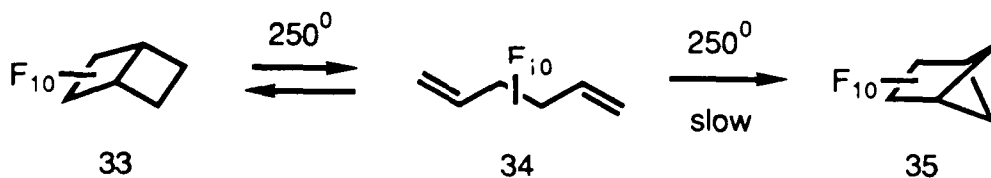
**31** X = H, Y = F

**32** X = Y = F

triene system of a 1,3,5-cyclooctatriene brings about only modest change in either the equilibrium constant or the height of the barrier for cyclization, but that  $K_{eq}$  is influenced strongly by the extent of fluorination of the saturated carbons. The equilibrium constant is  $\sim 4300$  times larger for **32** than for **30**. In the pair of isomers **31** *exo/endo* isomerism comes into play. Here a much higher barrier for tub-tub interconversion was found in the triene than in the parent hydrocarbon, probably for steric reasons. The *exo*-H configuration of the derived bicyclic diene was found to be much stabler than the *endo* form, presumably because of smaller dipole-dipole repulsion among C-F bonds. Evidence has been adduced in this study that the controversial strain energy of octafluorocyclobutane is smaller than that of cyclobutane itself, but not dramatically so.

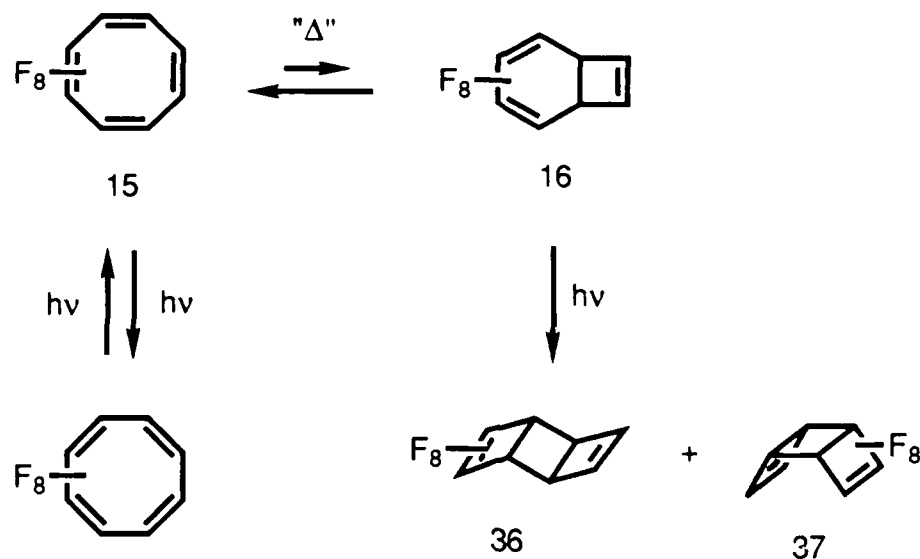
Paquette has shown that at high temperatures cyclooctatetraene undergoes degenerate skeletal rearrangement via internal Diels-Alder/*retro*-Diels-Alder reactions, as revealed by studies of labelled derivatives. In the hope of finding degenerate skeletal rearrangement in highly fluorinated analogs and elucidating its mechanism, we pyrolyzed the doubly labelled derivative **28** of perfluorocyclooctatetraene (**15**) under both static and flow conditions. Though a dimer was obtained whose structure is not yet fully elucidated, no evidence for skeletal rearrangement could be found under conditions which avoided rampant destruction of the tetraene system. Static pyrolyses at temperatures as high as  $3000^\circ$  were tolerated by **28**.

Prepared by direct fluorination of hexafluorodewarbenzene (**3**), decafluorobicyclo[2.2.0]hexane (**33**) ring opens slowly and reversibly at  $250^\circ$  to decafluorohexa-1,5-diene (**34**), which cyclizes more slowly yet to decafluorobicyclo[2.1.1]hexane (**35**). At  $325^\circ$  these reactions are quite rapid, and **35** is the exclusive product. These transformations highlight the contrasts in relative energy content of fluorocarbon valence isomers and their hydrocarbon counterparts, for in the hydrocarbon series both bicyclic isomers are transformed thermally into the diene in quantitative yield. The contrast is understandable in terms of the destabilization of carbon-carbon double bonds by heavy fluorine substitution.

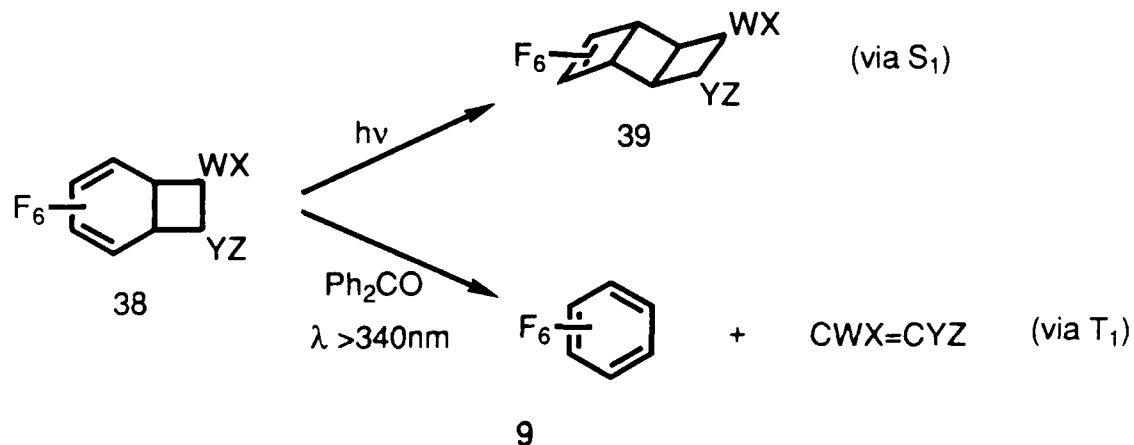


*Photochemical.* Ultraviolet irradiation of **28** at  $-30^{\circ}$  brought about rapid establishment of a photostationary state with its bond-shift isomer **29** at ambient temperature. It is thus likely that this process, which is invisible in the absence of a double label, occurs as well in the photochemistry of perfluorocyclooctatetraene (**15**).

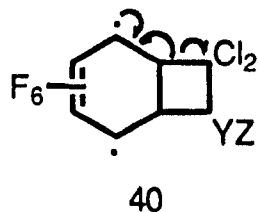
We discovered long ago that **15** photocyclizes to give a 20:1 mixture of tricyclooctadienes **36** and **37**, and our hypothesis that its bicyclic isomer **16** is an intermediate in this transformation is supported by the fact that **16** photocyclizes even at very low temperatures to **36**. Recently we showed that photocyclization of **15** is completely inhibited at  $-30^{\circ}$ , a temperature low enough to prevent thermal cyclization of **15** to **16**. We therefore believe that the first step in the photocyclization of **15** is actually a thermal one, and the overall sequence of events can be depicted as follows:



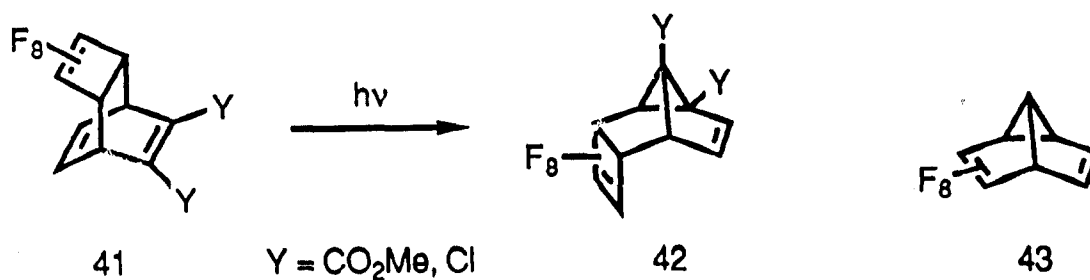
A brief study of the photochemistry of a series of bicyclooctatrienes (**38**) revealed an interesting dependence of the product composition on the nature of the reacting excited state. Direct excitation into the singlet manifold invariably resulted in facile cyclization, yielding tricyclic



derivatives **39**. On the other hand, triplet sensitization resulted in no reaction, cyclization, and/or fragmentation to hexafluorobenzene plus olefin, depending upon the substituents at C.7 and C.8. Fragmentation occurred when geminal chlorines were present, consistent with the interpretation that radical-stabilizing substituents on the two-carbon bridge make homolytic bond cleavage possible in the triplet state, as shown in **40**.



Finally, tricyclic trienes **41** were prepared from cyclooctatetraene **15** and their photochemistry was examined. Both were found to undergo di-pi-methane rearrangement, yielding **42**. This finding opens up a new synthetic approach to a molecule which has eluded a variety of synthetic attempts in our laboratory, octafluorosemibullvalene (**43**), for **42** incorporates the semibullvalene skeleton.



### Publications Based on AFOSR-Supported Work

- Rahman, M. M.; Lemal, D. M.; Dailey, W. P. "Negative Hyperconjugation. The Rotation-Inversion Barrier in alpha-Fluoramines", *J. Am. Chem. Soc.* **1988**, *110*, 1964-6.
- Dailey, W. P.; Correa, R. A.; Harrison, E., III; Lemal, D. M. "The 5,6-Dichlorohexafluorocyclohexa-1,3-dienes: Hexafluorobenzene Synthons", *J. Org. Chem.*, in press.
- Soelch, R. R.; McNierney, E.; Tannenbaum, G. A.; Lemal, D. M. "The Synthesis and Chemistry of Highly Fluorinated Bicyclo[2.2.0]hexenones", *J. Org. Chem.*, in press.
- Dailey, W. P.; Ralli, P.; Wasserman, D.; Lemal, D. M. "Cycloadditions of *cis*-5,6-Dichlorohexafluorocyclohexa-1,3-diene", *J. Org. Chem.*, in press.
- Spector, T.; Rahman, M. M.; Shafer, P. R.; Lemal, D. M. "Bond-Shift Isomerization of Heptafluorocyclooctatetraene", *J. Am. Chem. Soc.*, submitted for publication.

### Manuscripts in Preparation

- Rahman, M. M.; Secor, B. A.; Morgan, K. M.; Shafer, P. R.; Lemal, D. M. "Valence Isomerization Equilibria of Highly Fluorinated Cycloocta-1,3,5-trienes" (*J. Org. Chem.*)
- McCoy, C. H.; Lemal, D. M. "A Convenient New Method for Cyclopropanation with Dibromocarbene" (*J. Org. Chem.*)
- Klopotek, D. L.; Wilterdink, J. L.; Lemal, D. M. "Derivatives of Tetrafluorocyclopentadienone" (*J. Org. Chem.*)

Work is complete, or in some cases nearly so, for several additional manuscripts.

### Coworkers

#### Postdoctoral Associate

Rahman, M. M.

#### Graduate Students

Correa, R. A.

Jensen, B. A.

Kendall, J.

Spector, T.

Takenaka, N.

## Theses and Degrees Awarded

### Ph. D.

Spector, T., Part I. "Approaches to the Synthesis of Tetracyanocyclobutadiene Dianion" Part II. "Synthesis and NMR Investigation of Perfluorocyclooctatetraene Derivatives", 1987

### B. A.

Goldman, G. D., Part I. "Attempted Synthesis of Tetrakis(pentafluoroethyl)tetrahedrane" Part II. "Thermal and Photochemical Behavior of 1,2-Dichloroperfluorocyclooctatetraene", 1987

McCoy, C.H., "A Study of the Tribromoacetate Decomposition Method and a Novel Way of Generating Dibromocarbene", 1987

Morgan, K. M., "Negative Hyperconjugation. The Influence of Methoxy Substitution on a Fluorocarbon Isomerization Equilibrium", 1988

Roberts, B. E., Part I. "State-Dependent Photochemistry of Highly Fluorinated Bicyclo[4.2.0]octa-2,4-dienes" Part II. "A Search for High Temperature Degenerate Rearrangement of Highly Fluorinated Cyclooctatetraenes", 1989

Salsgiver, C. H., "Divergent Pathways in the Halogenation of Octafluorocyclooctatetraene", 1988

## Invited Lectures on AFOSR-Grant-Related Work

### At Universities

Worcester Polytechnic Institute	November, 1986
Bowdoin College	February, 1987
North Carolina State University	March, 1987
Bowling Green State University	November, 1987
Wabash College	November, 1987
West Virginia State University	February, 1988
Hamilton College	February, 1988
University of Iowa	October, 1988
North Dakota State University	October, 1988
University of Minnesota	October, 1988

### At Industrial Companies

Wyeth-Ayerst Laboratories	February, 1988
3M Corporation	October, 1988

At Meetings

American Chemical Society National Meeting, New York	April, 1986
New York Academy of Sciences	January, 1987
Twelfth International Symposium on Fluorine Chemistry	August, 1988

**Presentations by Coworkers**

Klopotek, D. L., contributed paper at the Twelfth International Symposium on Fluorine Chemistry, August, 1988

Jensen, B. A., poster presentation at the Ninth Winter Fluorine Conference, February, 1989

Takenaka, N., poster presentation at the Ninth Winter Fluorine Conference, February, 1989