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STRUCTURE AND REACTIVITY OF PERFLUORINATED ANNULENES
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AFOSR-83-0047

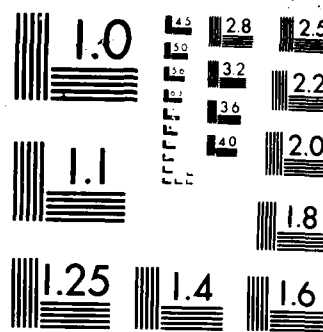
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FIELD	GROUP	SUB. GR.													
19. ABSTRACT (Continue on reverse if necessary and identify by block number) This report records the synthesis of an array of compounds representing many structural types, but all related to perfluorinated annulenes in the C₃ to C₁₀ range. Chemical reactivity of many of these compounds is described, together with equilibrium studies and kinetic investigations of isomerization, automerization and conformational interconversion processes. This research has increased considerably our knowledge of the effects of fluorine substitution on reactivity in organic molecules. Development of methodology which should be of general use in the synthesis of highly fluorinated compounds is discussed. OTC FILE COPY STIC EXTRACTE FEB 24 1987															
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Period Covered: January 1, 1983 to March 31, 1986

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

Principal Investigator: David M. Lemal

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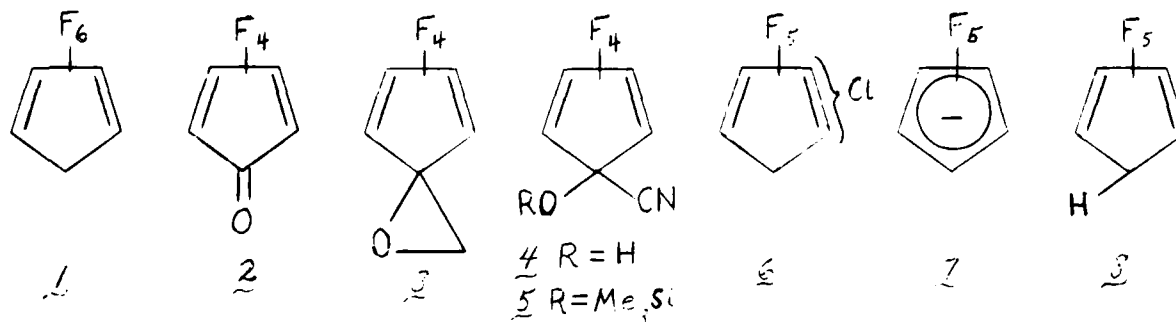
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Summary of Accomplishments

Many new fluorocarbons and fluorocarbon derivatives have been synthesized in the course of our investigation supported by the the grant AFOSR-83-0047. Some new synthetic methodology has been developed along the way. Studies of various kinds -- spectroscopic, equilibrium and kinetic -- have been carried out on many of the target molecules. Together with lessons from the synthetic work, these studies have increased considerably our knowledge of the effects of fluorine substitution on chemical reactivity and on the shapes of potential energy surfaces for various sets of valence isomers. The work has opened up numerous avenues for further investigation and has set the stage for significant advances in both the synthetic and physical organic aspects of organofluorine chemistry. The following concise summary of our research is organized according to compound types, presented roughly in order of increasing size of the carbon skeleton.

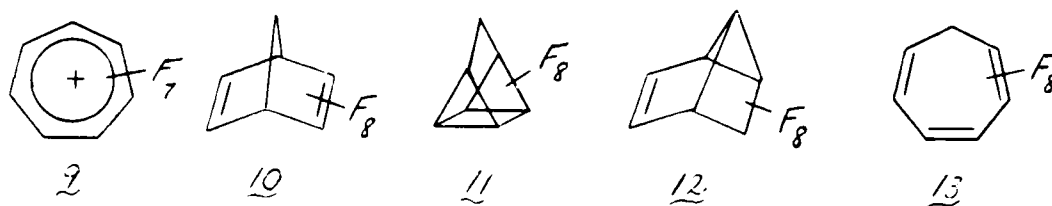
Highly fluorinated cyclopentadienes. New synthetic methods based on pyrolytic decarbonylation have been developed for hexafluorocyclopentadiene (**1**) and tetrafluorocyclopentadienone (**2**). The former is a useful diene which has been quite inaccessible because highly specialized equipment -- no longer needed -- has been required for its synthesis. The latter had been synthesized earlier in our laboratory, but is now available in just two steps from pentafluorophenol. The utility of dienone **2** as a building block in synthesis is limited by its extremely facile dimerization. To circumvent this problem, we have blocked the carbonyl group, leaving the diene system intact for subsequent cycloaddition reactions. Spiro derivative **3**, cyanohydrin **4** and protected cyanohydrin **5** have been prepared; the last, which is stable, quite resistant to dimerization and easy to deprotect, promises to be useful as a synthetic equivalent of dienone **2**. The pyrolytic decarbonylation route we have employed to prepare **1** and **2** has also made 1- and 2-chloropentafluorocyclopentadiene (**6**) readily available.

Because of the potentially great importance of the pentafluorocyclopentadienyl ligand in organotransition metal chemistry, we devoted much effort to the synthesis of the pentafluorocyclopentadienyl anion (**7**) and its conjugate acid 5H-pentafluorocyclopentadiene (**8**). We were ultimately successful, but during the course of our work Seppelt (Berlin) reported the synthesis of these species, albeit in low yield, via a different route. The most practical route may turn out to be a combination of the two.

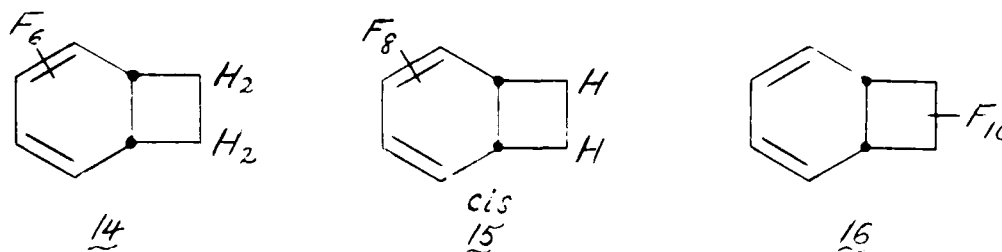


Heptafluorotropylium ion and heptafluorotropilidene valence isomers.

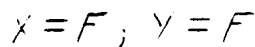
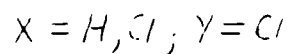
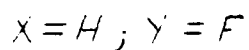
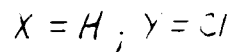
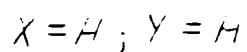
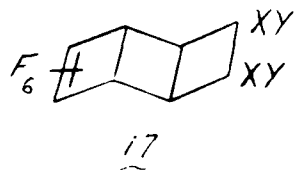
Among our most interesting discoveries was a serendipitous synthesis of the previously unknown heptafluorotropylium ion (**9**). Having developed a new route to octafluoronorbornadiene (**10**), we found that ultraviolet irradiation transformed it into the new octafluoroquadricyclane (**11**). Remarkably, warming of **11** above 0° results in the formation of tricycloheptadiene **12**, which undergoes further rearrangement at room temperature to give octafluorotropilidene (**13**). This triene readily gives up a fluoride ion to a Lewis acid, yielding the ion **9**. Many gas- and condensed-phase studies of this interesting ion are planned. The extraordinary lability of highly strained fluorocarbons **11** and **12** has inspired us to undertake further studies, two of which are discussed below, of the destabilizing effects of fluorine substitution on cyclopropane rings.



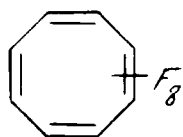
Highly fluorinated bicyclo[4.2.0]octadienes: valence isomerism. Systems capable of valence isomerization present a special opportunity for observing the effects of substituents, for they permit facile and accurate determination of the relative energies of related structures without recourse to difficult and inherently less accurate thermochemical studies. With this in mind, we have synthesized bicyclooctadienes **14-16** and examined their equilibria with the corresponding monocyclic valence isomers (cyclooctatrienes). For both **14** and **15** the equilibrium



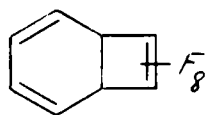
constant is not far from unity, but the bicyclic form so dominates the equilibrium in the case of **16** that no cyclooctatriene has been detected. This contrast is probably related to the recently discovered fact that perfluorocyclobutane enjoys an anomalously small strain energy for reasons which are not yet clear. The synthesis of **14-16** was made possible by new photocycloaddition reactions involving hexafluorobenzene. Adducts **17** have been prepared by ultraviolet irradiation of the benzene with appropriately substituted ethylenes.



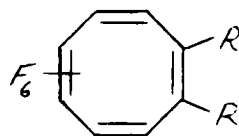
Highly fluorinated cyclooctatetraenes: equilibria and dynamics. Cyclooctatetraene and many of its derivatives are capable of undergoing three dynamic processes at ordinary temperatures: electrocyclization to a bicyclic form, bond-shift isomerization and tub inversion. We were able to synthesize independently the bicyclic form (octafluorobicyclo[4.2.0]octatriene, **19**) of octafluorocyclooctatetraene (**18**) and determine the activation parameters for the conversion of this very labile liquid (half-life, 14 min at 0°) to the stabler tetraene **18**. At room temperature we found the equilibrium constant for $\mathbf{18} \rightleftharpoons \mathbf{19}$ to be 3×10^{-3} , a much larger value than that for the parent hydrocarbons.



18

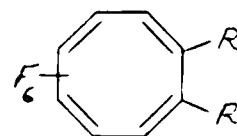


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20 $R = Cl$

22 $R = H$



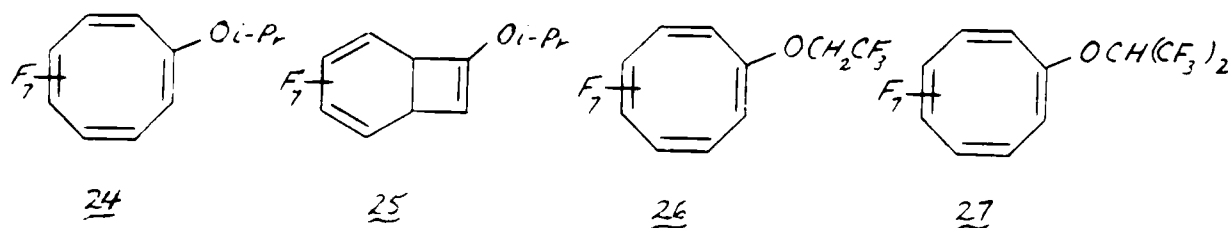
21 $R = Cl$

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Studying the other dynamic processes in octafluorocyclooctatetraene requires incorporation of a label, since they are degenerate changes. Our finding that 1,2-dichlorohexafluorocyclooctatetraene (**20**) undergoes essentially irreversible bond-shift isomerization to the 1,8-isomer **21** only slowly at temperatures well above 100° indicated a barrier height of >30 kcal./mole, nearly twice that for cyclooctatetraene itself. On the other hand, synthesis at room temperature of 1H,2H-hexafluorocyclooctatetraene (**22**) yielded only the 1H,8H-isomer (**23**), indicating that the initially formed target molecule had spontaneously isomerized under very mild conditions. Presumably the difference in size between chlorine and hydrogen is responsible for this contrast. We then guessed

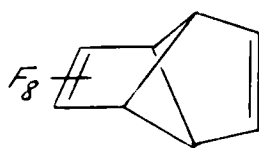
that the barrier for the octafluoro compound would lie within reach of dynamic NMR methodology, which requires only monosubstitution (and thus minimal perturbation) to reveal bond-shift isomerization.

Accordingly, we synthesized the isopropoxy derivative **24**, believing that the small, highly electronegative oxygen would be similar enough to fluorine to cause little change in the molecular dynamics. We were thus very surprised to find that bicyclic isomer **25** was the dominant form at equilibrium in all solvents. In acetone the equilibrium constant for electrocyclization was 700 times greater than in the octafluoro system! None of the other three bicyclic isomers was detectable. The equilibrium was very solvent-dependent, polar solvents favoring the bicyclic form. Several years earlier we had synthesized partially fluorinated alkoxy derivatives **26** and **27**, and a reexamination of their spectra revealed minor amounts of a bicyclic form. Since the fraction of bicyclic form at

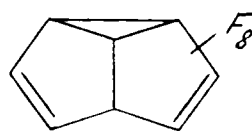


equilibrium diminishes sharply in the series **24** > **26** > **27**, i.e. as electron withdrawal by the alkyl group increases, it appears that the ability of oxygen to donate a lone pair to the attached double bond is responsible for the shift in equilibrium toward bicyclic isomers. This intriguing observation will be the subject of further study, as we believe it may shed light on the controversial subject of negative hyperconjugation. Isopropoxy derivative **24** has proven to be interesting for other reasons as well: spin-saturation transfer experiments have revealed both bond-shift isomerization and (by virtue of the diastereotopic methyls) tub inversion in this molecule. Accurate barriers are not yet available because of the complexity of analyzing a system undergoing three simultaneous dynamic processes, but it is clear that 1) electrocyclization and tub inversion have similar barriers, with that for bond-shift isomerization significantly higher and 2) the barriers for the two automerizations are much higher than in the parent cyclooctatetraene.

Approaches to tricyclo[3.3.0.0^{2,6}]octa-3,7-diene and octafluorosemibullvalene. Considerable theoretical interest attaches to both of these tricyclic octadienes: to the first (**28**) by virtue of conjugation of the double bonds mediated by the Walsh orbitals of the central cyclobutane ring, and to the semibullvalene (**29**) by virtue of its presumably very low (possibly nonexistent!) barrier for degenerate Cope rearrangement. Both compounds have presented a

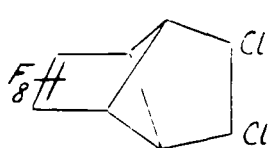


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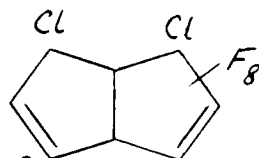


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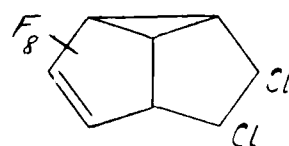
difficult synthetic challenge which has not yet been overcome, apparently because they are very delicate. They are considered here together because the general strategy we have used for synthesizing **29** entails construction of the carbon skeleton of **28**, then facile thermal rearrangement at an appropriate stage to that of **29**. Much has been learned about how **28** and **29** cannot be made; in the process new ideas for their synthesis have emerged, and the quest continues. Structures **30-35** are a few of the new compounds which have been synthesized (all



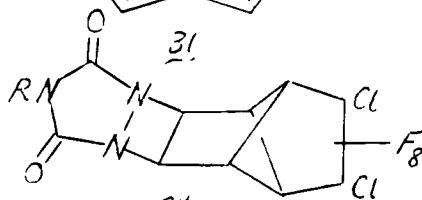
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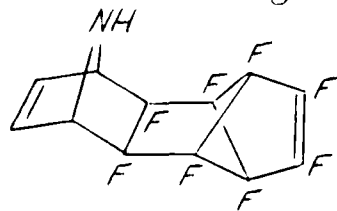


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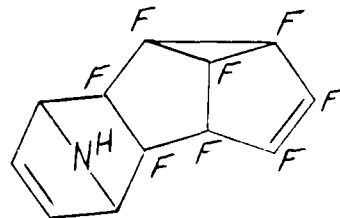


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$R=CH_3, C_6H_5$



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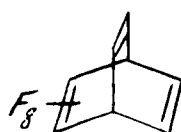


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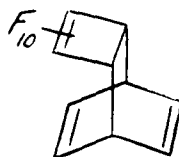
from hexafluorobenzene) in connection with this problem. Pentacyclic compounds **34** are very unusual among triazolidinedione adducts because they exhibit endo-exo isomerization by virtue of nitrogen inversion. This strongly solvent-dependent phenomenon is observable on the NMR time scale at room temperature. At temperatures as low as 130° compound **35**, formally the Diels-Alder adduct of **29** with pyrrole, undergoes retrocycloaddition. However, the reaction yields, not semibullvalene **29**, but its very stable valence isomer octafluorocyclooctatetraene (**18**).

Other strained fluorocarbons. We have been able to synthesize another interesting valence isomer of tetraene **18** from hexafluorobenzene: octafluorobarrelene (**36**). This molecule

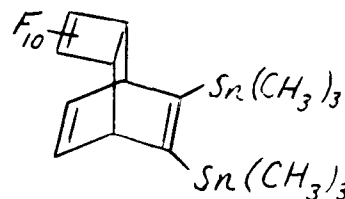
incorporates cyclic conjugation of an unusual sort which should have important consequences for both its spectra and its chemical reactivity. We had hoped that this molecule would serve as a photoprecursor for semibullvalene **29**, in analogy to the behavior of its hydrocarbon counterpart, but both sensitized and direct photolyses of the barrelene have yielded only the stable tetraene **18**.



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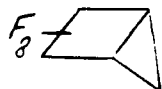
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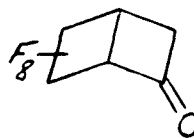
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No member of the $(CF)_{10}$ valence isomer set has yet appeared in the literature. As an initial entree to this potential energy surface we chose decafluoro Nenitzescu's hydrocarbon (**37**). We have been able to prepare quite efficiently an immediate precursor for this molecule, the nicely crystalline tin-containing tricycle **38**. In addition, we have strong spectroscopic evidence for the target compound **37** in the reaction product from direct fluorinolysis of the carbon-tin bonds in **38**. Unfortunately, a serious accident involving tin poisoning cut short the work on this problem, which will be taken up again in the future. Since we regard **37** as a potential source of various other $(CF)_{10}$ valence isomers via thermal and photochemical transformations, its isolation and purification have a high priority.

We have also attempted to synthesize octafluorobicyclo[2.1.0]pentane (**39**), a highly strained fluorocarbon which is expected to undergo facile "ring-flapping" isomerization involving cleavage of the central bond. The barrier for this process, which we hope will be accessible to dynamic NMR methodology, is of interest in connection with the effect of fluorine substitution on strain in three- and four-membered rings. Our synthetic efforts, which were based on photodecarbonylation of octafluorobicyclo[2.2.0]hexan-2-one (**40**) as the final, key step, were unrewarded because of the tendency of strained intermediates along the route to suffer fragmentation reactions. From these frustrations have emerged ideas for a promising new approach which is currently being pursued.



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40

It is worthwhile noting that some advances in synthetic methodology have been made in the course of the work described above. None of the methods cited here were invented by us, but we have developed them and demonstrated their generality and usefulness in fluorocarbon synthesis. The combination of zinc dust, dimethyl sulfoxide and ultrasound has proved to be a powerful method for vicinal dechlorination and debromination of halofluorocarbons. It made possible the synthesis of the extremely labile triene **19**, for example, and led to a considerably improved synthesis of tetraene **18**. The latter is used in large quantities by R. P. Hughes' group for organometallic research as well as by our own group.

A second advance was the finding that addition of bis(trimethylstannyl)acetylene to fluorinated dienes (discovered by Haszeldine) is quite general and that the stannyl groups in the adducts can be replaced by fluorines by direct fluorinolysis in acetonitrile. Thus, the tin-substituted acetylene functions as a synthon for the extremely labile and synthetically useless difluoroacetylene, making possible the construction of new fluorocarbon skeletons (e.g. **36** and **37**).

Finally, we have found that highly fluorinated cyclopentadienes and tetrafluorocyclopentadienone can be prepared by decarbonylation under flow pyrolysis conditions of cyclohexadienones and tetrafluoro-*o*-quinone, respectively. It appears that this route is quite general, and its attractiveness is enhanced by the ready availability of appropriate starting materials from benzenes.

Publications

Laganis, E. D.; Janik, D. S.; Curphey, T. J.; Lemal, D. M. "Photochemistry of Perfluoro-3-diazo-2-butanone", *J. Am. Chem. Soc.* **1983**, *105*, 7457. (work completed before the beginning of the AFOSR grant)

Walther, B. W.; Williams, F.; Lemal, D. M. "The Octafluorocyclooctatetraene Radical Anion. Identification and Proof of Aromaticity by Electron Spin Resonance", *J. Am. Chem. Soc.* **1984**, *106*, 548. (work carried out before the beginning of the AFOSR grant)

Dailey, W. P.; Lemal, D. M. "Perfluorotropilidene Valence Isomers and the Perfluorotropylum Ion", *J. Am. Chem. Soc.* **1984**, *106*, 1169.

Waldron, R. F.; Barefoot, A. C., III; Lemal, D. M. "Perfluorobicyclo[4.2.0]octa-2,4,7-triene, a Labile (CF₈) Valence Isomer", *J. Am. Chem. Soc.* **1984**, *106*, 8301.

Soelch, R. R.; Mauer, G. W.; Lemal, D. M. "New Routes to Hexafluorocyclopentadiene and Related Compounds", *J. Org. Chem.* **1985**, *50*, 5848.

Other work carried out during the grant period is ready for publication, and some of the writing has been done. Many of the projects described in the report, however, are not yet finished. While it would be possible to publish much of this research in preliminary form, we wish to complete the work fully first. We plan to bring several of these projects to fruition in the near future.

Coworkers

Postdoctorals

Klopotek, D. L. (on sabbatical from St. Norbert College)

Ralli, P.

Graduate Students

Dailey, W. P.

Mauer, G. W.

Sharos, C. S.

Soelch, R. R.

Spector, T.

Technician

Hamlin, R. E.

Theses and Degrees Awarded

Ph. D.

Dailey, W. P., "Synthesis of Potentially Möbius Aromatic Heterocycles", 1983

Mauer, G. W., "Part 1. Synthesis and Chemistry of Fluorinated Cyclopropenes. Part 2.

The Excited State in Polycyclic Aromatic Hydrocarbon Photochemistry", 1983

Soelch, R. R., "The Synthesis and Chemistry of Highly Fluorinated Cyclopentadienes", 1984.

B. A.

Cohen, T. D., "A New Synthetic Pathway Toward Perfluorotropylium Ion and a Thermodynamic and Kinetic Study of the Vicinal Dichlorohexafluorocyclooctatetraenes", 1985

DiFiore, J. W., "A Synthetic Approach to the Valence Isomers of Perfluorocyclooctatetraene", 1983

Kallman, J. E., "Further Steps Toward Perfluorosemibullvalene: Synthesis of 1-Bromo-1,2-dichlorodifluoroethane", 1986

Raymond, J. F., "Toward the Synthesis of a Polyfluorinated Bicyclo[2.1.0]pentane", 1985

Secor, B. A., "The Valence Isomerizations of Perfluorobicyclo[4.2.0]octa-2,4-diene, 7,8H-perfluorobicyclo[4.2.0]octa-2,4-diene, and 7,7,8,8H-perfluorobicyclo[4.2.0]octa-2,4-diene", 1985

Sharos, C. S., "Approaches to the Synthesis of Organofluorine Compounds", 1983

Steffen, M. A., "In Quest of Perfluorosemibullvalene", 1985

Waldron, R. F., "The Valence Isomerization of Octafluorocyclooctatetraene", 1984

Wilterdink, J. L., "Part 1. Attempted Synthesis of a Dewar Phosphole. Part 2. A Perfluorocyclopentadienone Synthon", 1984.

Invited Lectures on AFOSR-Grant-Related Work

At Universities

Univ. of Illinois	April, '83
Univ. of Maryland	April, '83
University of Tennessee	April, '83
Univ. of Western Ontario	March, '84

York Univ.	March, '84
McMaster Univ.	March, '84
Univ. of Waterloo	March, '84
Yale Univ.	April, '84
Middlebury College	October, '84
McGill Univ.	November, '84
Univ. of Massachusetts	May, '85
Tufts Univ.	October, '85
Clemson Univ.	November, '85

At Industrial Companies

Merck, Sharp and Dohme	April, '85
Smith Kline Beckman	September, '85

At Meetings

Gordon Research Conf. on Physical Organic Chemistry, Wolfeboro, N. H., June, '83
 American Chemical Society National Meeting, Washington, D. C., August, '83
 Winter Fluorine Conference, Orlando, Florida, February, '85
 American Chemical Society National Meeting, Miami, Florida, April '85
 American Chemical Society National Meeting, New York, N. Y., April, '86

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