to control the stereochemistry of product formation enhances the synthetic utility of these procedures. Further stereochemical studies in this area could shed light on geometrical considerations for likely metallazetidine intermediates.[9]

Acknowledgment. We acknowledge support for this work given by the National Science Foundation and the National Institutes of Health.

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(9) For aldehydes, only one isomer of the imine is noted; for the imidate, both *E* and *Z* isomers exist in comparable amounts,[10,11] and four metallazetidines are therefore possible.

(10) Deyrup, J. A.; Gingrid, H. L. *J. Org. Chem.* **1977**, *42*, 1015.

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Perfluorobicyclo[4.2.0]octa-2,4,7-triene: A Labile $(CF)_8$ Valence Isomer

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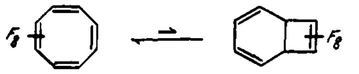
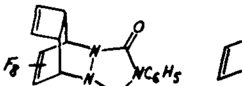
We wish to report the synthesis, characterization, and some of the chemistry of the title compound (**2**), the elusive bicyclic valence isomer of perfluorocyclooctatetraene (**1**). As is the case with cyclooctatetraene itself,[2] the bicyclic isomer is present in such small amount at equilibrium that it has never been detected directly in samples of the tetraene (eq 1). Its existence has been



1 2 (1)

implied, however, by the reaction of **1** with dienophiles to give adducts such as **3**,[3] which are (formally, at least) Diels–Alder adducts of **2**. In addition, ultraviolet irradiation of the tetraene yields a 20:1 mixture of tricyclo[4.2.0.0^{2,5}]octa-3,7-dienes **4** and **5**, a result most easily understood in terms of **2** as an intermediate (formed either thermally or photochemically).[4]



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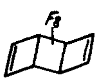
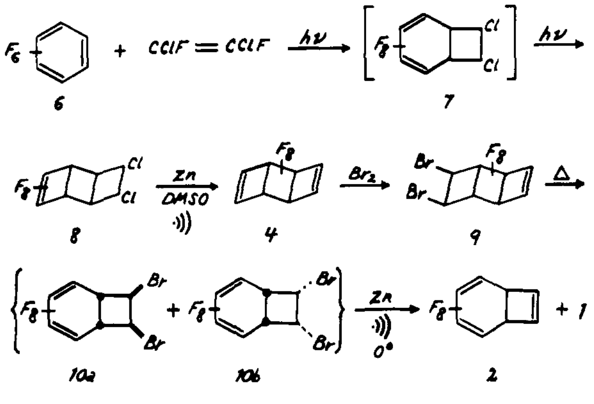


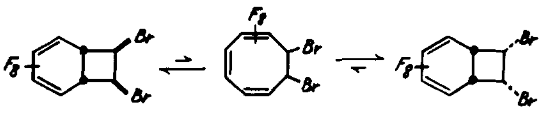
4

5

Scheme I



Starting with perfluorobenzene (**6**), we have now synthesized bicyclic triene **2** in five steps (Scheme I). Photocycloaddition of **6** to dichlorodifluoroethylene proceeded in [2 + 2] fashion to yield **7**, which photocyclized under the reaction conditions to give a stereoisomeric mixture of anti tricyclic adducts **8**.[5] Dechlorination of **8** was accomplished with activated zinc dust in dimethyl sulfoxide under the influence of ultrasound at room temperature and reduced pressure (58% yield after recrystallization from isopentane).[6] *We have found this combination to be remarkably effective for vicinal dechlorination of chlorofluorocarbons.*[9] The resulting *anti*-tricyclooctadiene **4** reacted stereospecifically with bromine to give the known cis,exo dibromide **9** together with the doubly cis,exo tetrabromide, from which it is easily separated.[4] Replacement of chlorines by bromines was essential in order that the final step in the sequence be performable under the mildest possible conditions. Thermolysis of **9** at 160 °C yielded an 87:13 mixture of stereoisomeric dienes **10a** and **10b** (95% after distillation). The presence of endo isomer **10b** reveals that the initially formed exo diene **10a** ring opened to monocyclic triene **11**, which recyclized to produce both dienes (eq 2). None of the monocyclic isomer could be detected in the product mixture.[10]



10a 11 10b (2)

At temperatures near 0 °C the major isomer **10a** crystallized, allowing separation from **10b**. Spectroscopic data for **10a**:[11] IR (neat) 1750, 1705, 1405, 1350, 1325, 1190, 1030, 850 cm^{-1}; UV (cyclohexane) λ_{max} 281 nm (log ϵ = 3.43); ^{19}F NMR (CDCl$_3$)[12] 123.5, 148.4, 154.6, 157.7 ppm, for **10b**, 126.6, 148.4, 154.6, 181.3 ppm.[13]

In the culminating step, **10** was debrominated with activated zinc dust in 1:1 dimethyl sulfoxide/*N*-methylpyrrolidinone in an ultrasonic bath at 0 °C and 0.05 torr. Under these conditions bicyclic triene **2** distilled as it was formed into a U-trap at −196 °C, together with a minor amount of tetraene **1**. With care an 82:18 mixture of triene/tetraene could be obtained in 74% yield. The identity of the bicyclic triene was revealed by the spectroscopic data described below and by its quantitative isomerization to perfluorocyclotetraene at subambient temperatures. Measured at −60 °C in methylene chloride, the ^{19}F NMR spectrum comprised four multiplets of equal area at 118.3 (F_7,F_8), 150.4 (F_3,F_4), 154.5 (F_2,F_5), and 159.1 ppm (F_1,F_6). The infrared spectrum, determined in an argon matrix at 20 K, revealed bands at 1773

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(6) This appears to be the first report of an ultrasound-assisted vicinal dehalogenation by zinc. The zinc/ultrasound combination has been used by others, however, to generate *o*-xylylene from α,α′-dibromo-*o*-xylene[7] and to prepare organozinc reagents.[8]

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(11) A satisfactory elemental analysis was obtained (Galbraith Laboratories, Inc., Knoxville, TN).

(12) Chemical shifts are reported in parts per million upfield from internal trichlorofluoromethane.

(13) The contrast in chemical shift of the bridgehead fluorines in the two isomers (157.7 vs. 181.3 ppm) forms the basis for the configurational assignment, as the lower field position is characteristic of bridgehead fluorines vicinal to exo bromines in perfluorotricyclo[4.2.0.0^{2,5}]octane derivatives.[4]

(4-ring C=C stretching), 1712 (diene C=C stretching), 1441, 1416, 1364, 1227, 1094, 1057, 969, 853, 788, 765, and 733 cm^{-1}. A structureless maximum appeared at 241 nm (log ϵ = 3.3 (1)) in the ultraviolet spectrum of the triene, determined at −60 °C in 95% ethanol. The hypsochromic shift relative to dibromide **10a** is striking.

The first-order rate of valence isomerization of the bicyclic triene **2** to **1** was measured in methylene chloride at several temperatures between 0 and −25 °C. These activation parameters were determined: $E_a = 18.9 \pm 0.6$ kcal/mol, $A = 1.1 \times 10^{12}$, corresponding to a half-life of 14 min at 0 °C. Remarkably, these numbers are indistinguishable from the values reported by Vogel[14] for the ring opening of the parent hydrocarbon ($E_a = 18.7 \pm 0.8$ kcal/mol, $A = 9.1 \times 10^{11}$, $t_{1/2}$ = 14 min at 0 °C). In light of the fact that extensive fluorine substitution dramatically alters properties and behavior of unsaturated hydrocarbons, this result was hardly a foregone conclusion. Its implications will be discussed after efforts in progress to measure the equilibrium constant for the **1**–**2** interconversion have been completed.

Irradiation of a methylene chloride solution of **2** at −50 to −60 °C with a superpressure mercury arc at wavelengths >220 nm produced the *anti*-tricyclooctadiene **4**.[15] This finding lends strong support to our earlier surmise that **2** is an intermediate in the photochemistry of **1**, though it does not, of course, require that conclusion. Photoisomerization of **2** to **4** also took place in an argon matrix at 20 K.

Cyclooctatetraene itself has been reported to photocyclize to its bicyclic isomer,[16] but no tricyclo[4.2.0.0^{2,5}]octa-3,7-diene has been obtained by irradiation of either isomer.[17]

Acknowledgment. We thank the Air Force Office of Scientific Research (AFOSR-83-0047) and the National Science Foundation (CHE-7924309) for generous support of this research.

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(14) Vogel's synthesis was also based on reduction of a dibromide (Vogel, E.; Kiefer, H.; Roth, W. R. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 44).

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Spectral Simplification and Improved Sensitivity in Magic Angle Sample Spinning NMR

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The magic angle sample spinning (MASS) NMR experiment[1-3] has become a popular approach for obtaining high-resolution spectra of dilute spins in solids. If the spinning speed (ν_R) is less than the breadth of the static chemical shift powder pattern $\Delta\sigma = \sigma_{11} - \sigma_{33}$, the pattern breaks up into a centerband at the isotropic frequency and sets of rotational sidebands spaced at integral multiples of the rotor frequency. However, this approach to high resolution suffers from two deficiencies. First, since the observed signal intensity is now shared among the centerband and sidebands, the sensitivity of the experiment is decreased. Second, sidebands of one resonance may overlap with those from another, making interpretation of the spectrum difficult. Two approaches have been reported for dealing with these problems,[4,5] but both partially fail when $\Delta\sigma/\nu_R$ is large. In this paper we document these shortcomings and introduce a new technique for attenuating sidebands without significant intensity losses.

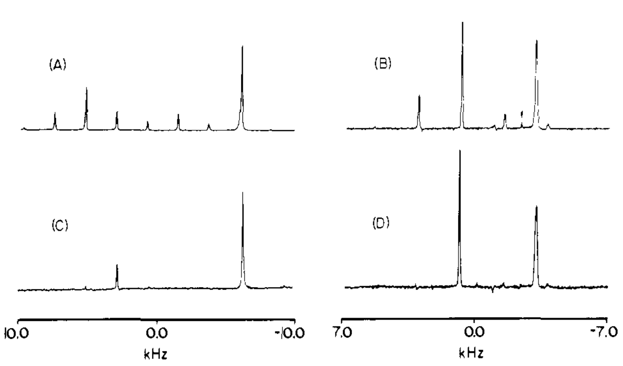

Figure 1. (A) MASS spectrum of HMB obtained at 79.9 MHz with ν_R = 2.27 kHz. The low-frequency line is due to the methyl carbons. The centerband of the aromatic resonance is denoted by an *, and contains 20% of the total integrated intensity. (B) HMB spectrum obtained with scaling (scale factor = 0.5) at ν_R = 2.27 kHz. The centerband of the aromatic resonance contains 70% of the total integrated intensity. Three weak sidebands are visible. The line denoted with a ‡ is a rotor frequency line. (C) HMB spectrum obtained with the same spinning speed by using TOSS. Sidebands are attenuated but the TOSS peak contains only 22% of the total integrated intensity. (D) HMB spectrum obtained with the same spinning speed using the new technique. The aromatic line contains 83% of the total integrated intensity.

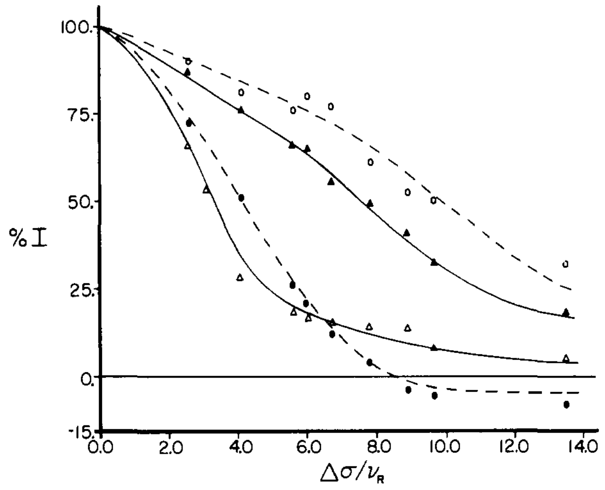

Figure 2. Experimental results showing the percentage of the total intensity contained in the centerband in the TOSS (●), MASS (△), scaled (▲), and new (○) experiment as a function of $\Delta\sigma/\nu_R$. The solid and dashed curves are the result of numerical calculations using a computer program described elsewhere.[8]

The first approach for dealing with rotational sidebands uses a multiple-pulse experiment to scale shift anisotropies by a predetermined factor.[5,6] If the anisotropies are reduced so that they are comparable to the rotor frequency, then any remaining sidebands will be very weak. Figure 1A shows a MASS spectrum of hexamethylbenzene (HMB) where the aromatic resonance consists of a centerband (*) and six sidebands. Figure 1B shows a spectrum obtained with the scaling experiment. Since the

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