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exo,exo-4,8-Ethenopolyfluoro-2,6-dioxaperhydroindacenes. Unusual Alkenes Flanked with Fluorine Atoms

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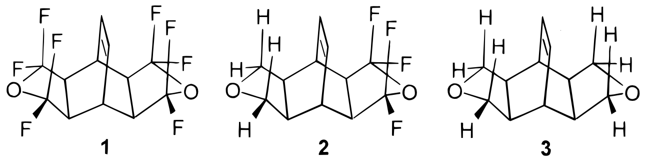
Unusual alkenes, *exo,exo*-4,8-etheno-1,1,3,3,5,5,7,7-octafluoro-2,6-dioxaperhydro-*s*-indacene (**1**) and *exo,exo*-4,8-etheno-1,1,3,3-tetrafluoro-2,6-dioxaperhydroindacene (**2**), as well as their nonfluorinated analogue **3** were synthesized. The structures of **1** and **3** have been determined in the solid state by X-ray crystallography and of all three compounds in solution by ^{1}H, ^{19}F, and ^{13}C NMR spectroscopy. The chemical properties of compounds **1**−**3** were investigated and compared. The double bond in fluorinated polycycloalkenes **1** and **2** was found to be totally inert toward bromination, hydrogenenation, and oxidation with *m*-chloroperbenzoic acid and ozone. This is in contrast to nonfluorinated indacene **3**, which behaves like a normal alkene, readily adds bromine and hydrogen, and reacts with oxidants. The only successful chemical transformation of **1** was achieved by treatment with Mn_2O_7, which led to oxirane **15** and rearranged pentacyclic acetal **16**. An interesting skeletal rearrangement occurred in the course of bromination of **3** leading to bicyclic tetrabromo derivative **12**. High chemical inertness of polyfluoroindacenes **1** and **2** has been attributed mainly to through-space electronic interactions of the double bond with proximal fluorine atoms.

Introduction

Alkenes, due to their high reactivity, are commonly used intermediates in organic synthesis. However, there is growth in the number of unsaturated compounds that, in spite of their retarded or specific reactivities, attract considerable attention by investigators. These are sterically hindered alkenes substituted with bulky groups or strained fragments shielding the double bond. The general property of compounds of this type is chemical inertness of the double bond or a behavior significantly different as compared with usual alkenes. The synthesis, structure, and chemical properties of such systems have been described in detail in the recent review.[1]

Interesting chemical and spectral properties were also reported for polycyclic alkenes, *e.g.*, $[4\pi + 2\pi]$ adducts of anthracene with dienophiles, in which the double bond was flanked from one or both sites with proximal aromatic rings.[2] These functionalities could be arranged "parallelly" as well as "orthogonaly" in close proximity enabling direct $\pi{-}\pi$ interactions. Typical behavior of such compounds is either the lack of reactivity or unconventional reactions like substitution of a vinylic proton with deuterium or a halogen.

Chart 1



1 **2** **3**

In this paper, we report synthesis, structure, and spectral and chemical properties of a new type of unusual alkenes, *exo,exo*-4,8-etheno-1,1,3,3,5,5,7,7-octafluoro-2,6-dioxaperhydro-*s*-indacene (**1**) and *exo,exo*-4,8-etheno-1,1,3,3-tetrafluoro-2,6-dioxaperhydroindacene (**2**), behaving similarly to both of the above-cited classes of compounds (Chart 1). The characteristic structural feature of these new compounds is flanking the double bond with four or two proximal fluorine atoms. For the comparison, nonfluorinated analogue **3** was also synthesized, and its properties were investigated.

The syntheses of compounds **1** and **2** as well as their precursor **5** were based on the well-established reactions of 1,2-dicarboxylic acids or anhydrides with sulfur tetrafluoride leading to predominant or exclusive formation of the 2,2,5,5-tetrafluorotetrahydrofuran ring.[3]

Results and Discussion

Syntheses of Compounds 1−3 (Scheme 1). Attempted direct preparation of **1** by treatment of commercially available bicyclo[2.2.2]oct-7-ene-*exo*-2,3,5,6-tetracarboxylic dianhydride (**4**) with sulfur tetrafluoride and anhydrous hydrogen fluoride failed; a complex mixture was formed from which no individual product could be isolated. An alternative approach from the one-side fluorinated anhydride **5**, prepared in a different way,[4] gave compound **1** in a 64% yield and as the only product, which was purified by vacuum sublimation and recrystallization.

Compounds **2** and **3** were obtained in 21 and 34% overall yields from anhydrides **5** and **4**, respectively, by following a literature strategy of the construction of a tetrahydrofuran ring.[5] The syntheses included acidic methanolysis of anhydrides **5** and **4** followed by reduction of diester **6** and tetraester **8** to diol **7** and tetraol **9** and, finally, dehydration of the latter with $KHSO_4$. Nonfluorinated compound **3** was claimed to be obtained previously as a side product of the tosylation of tetraester **8**,

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† Polish Academy of Sciences.

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(1) Lerman, B. M. *Russ. Chem. Rev.*, **1995**, *64*, 1 (translation from *Uspekhi Khimii* **1995**, *64*, 3).

(2) Butler, D. N.; Gupta, I.; Wong Ng,W.; Nyburg, S. C. *J. Chem. Soc., Chem. Commun.* **1980**, 596 and references therein.

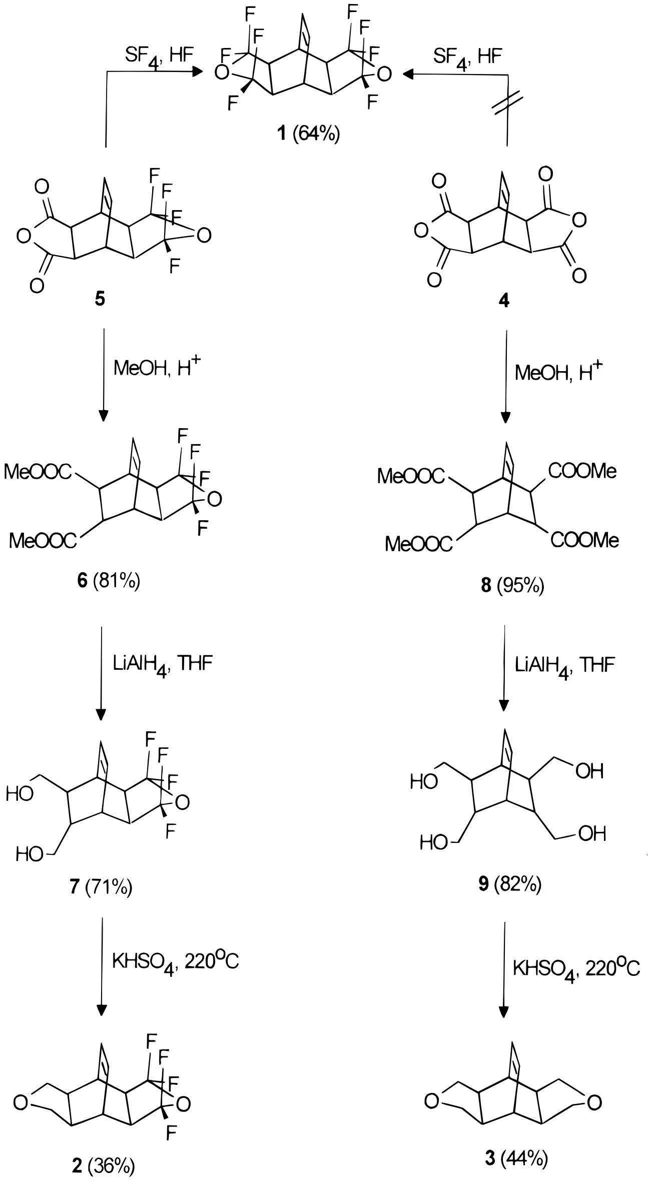
(3) (a) Dmowski, W.; Koliński R. *Polish J. Chem.* **1978**, *52*, 71. (b) Dmowski, W. *J. Fluorine Chem.* **1993**, *65*, 139. (c) Dmowski, W. *Polish J. Chem.* **1994**, *68*, 2175. (d) Dmowski, W.; Nowak, I.; Jones, P. G.; Thönnessen, H. *J. Fluorine Chem.* **1996**, *76*, 127.

(4) Nowak, I.; Dmowski, W. *J. Fluorine Chem.* in press.

(5) (a) Jamrozik, J. *Monatsh. Chem.* **1980**, *111*, 643; **1985**, *116*, 229. (b) Jamrozik, J.; Żesławski,W. *Monatsh. Chem.* **1992**, *123*, 129. (c) Jamrozik, J.; Jamrozik, M.; Ściborowicz, P; Żesławski, W. *Monatsh. Chem.* **1995**, *126*, 587.

(6) Dadet, M.-H.; Lhomme, J. *C. R. Acad. Sci. Paris, Ser. C* **1977**, *284*, 427.

Scheme 1



but no spectral data were reported, and the cited melting point was 80 °C higher from that of our compound.[6]

Structure and Spectral Properties of 1−3. X-ray crystallographic analyses were performed for octafluoroindacene **1** and its nonfluorinated analogue **3**. The results showed rigid *exo,exo* conformations for both compounds (Figures 1 and 2). Two independent molecules were found for **3** that superimpose one on another as the result of crystals packing in a cell. Compounds **1** and both forms of **3** have slightly distorted C_{2v} symmetry. Comparison of the bond lengths and bond angles in compounds **1** and **3** leads to the conclusion that the substitution of eight hydrogens by fluorines does not have a noticable influence on the shape of these molecules. The most evident difference is that the two tetrahydrofuran rings in **1** are more flat than those in **3** by *ca.* 6.8°; the average values for angles between the −C−O−C− planes and the four carbon atoms planes were found to be, respectively, 158.5° and 151.7°. The dihedral angles between the tetrahydrofuran rings and the cyclohexane rings, *e.g.*, C2−C3−C11−C10, differ only slightly, and the average values are 121.6° for **1** and 123.7° for **3**. No difference in the length of the double bond (C13−C14) was observed: 1.314 Å for **1** and 1.312 Å for **3** (average for two forms of **3**). The four fluorine atoms (Figure 1, F21, F62, F82, and F122) in **1** and also the corresponding four hydrogens in **3** form well-defined planes; the average deviation from the weighted least-squares planes does not exceed 0.039 Å for fluorines and 0.025 Å for protons. The ethylene bridge, in both **1** and **3**, is placed slightly over those planes by *ca.* 0.5 Å. Considering the results of crystallographic investigations and the similarity of the bulk of hydrogen and fluorine atoms (van der Waals radii are 1.20 and 1.35 Å, respectively),[7] it may be concluded that the C=C bond in both compounds **1** and **3** is located in similar steric environments. This statement is in accord with the general point of view that fluorine can replace hydrogen without notable steric consequence.

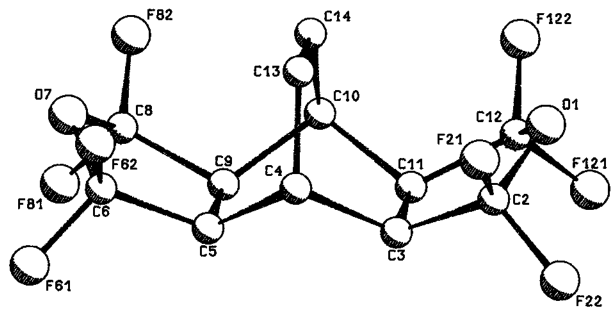


Figure 1. X-ray crystal structure of **1**. Hydrogen atoms are not shown.

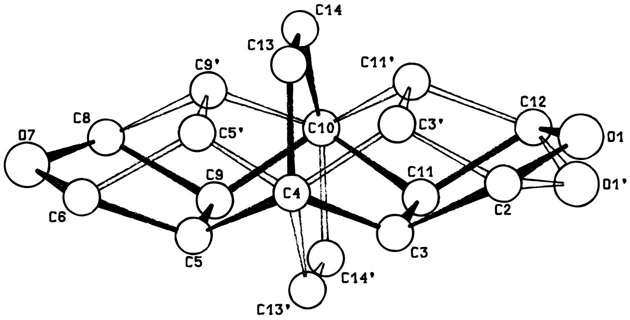


Figure 2. X-ray crystal structrure of **3** showing two superimposed molecules. Hydrogen atoms are not shown.

The high symmetry of molecules **1** and **3** is reflected by their NMR spectra. The ^{1}H NMR spectrum for **1** consists of only one signal for both vinylic protons and a complex multiplet for all other protons. Four signals deriving from protons of **3** were found: vinylic (2H), bridgehead (2H) and (4H), and an AB spin system for CH_2 groups. The ^{19}F NMR spectrum of **1** exhibits only two signals forming an AB spin system (J_{AB} = 146.7 Hz). The higher field signals (at −77.1 ppm) should be assigned to the fluorine that is placed close to the C=C bond. This is clear from the spectrum of compound **16** in which the higher field signal of one of the CF_2 groups shows evident “through-space” coupling to the ethylene bridge fluorine atom. The ^{13}C NMR spectra of both **1** and **3** consist of four signals, thus giving evidence for two symmetry planes. The signal of CF_2 group carbon atoms of **1** appears as a triplet with typical geminal carbon-to-fluorine coupling constants, 261 Hz. Couplings of the bridgehead carbon atom to CF_2 group fluorines through two and three bonds ($^2J_{CF}$ = 31.5, 21.2 Hz, $^3J_{CF}$ = 4.2 Hz) allows their assignment.

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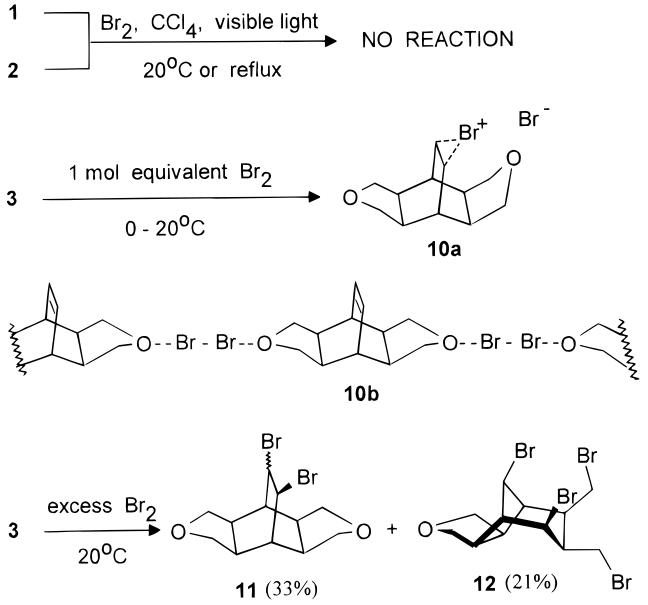
[7] (a) Pauling, L. *The Nature of the Chemical Bond and the Structure of Molecules and Crystals. An Introduction to Modern Structural Chemistry*, 3rd Ed.; Cornell University Press: Ithaca NY, 1960; p 260. (b) Bondi, A. *J. Phys.Chem.* **1964**, *68*, 441.

Scheme 2



No X-ray structure was obtained for compound **2** because of difficulties with growing a sufficiently well-shaped crystal; however, its structure has been unambiguously proven from the NMR spectra, which basically resemble that of **1**. The fluorine spectrum shows an identical AB system for CF_2 groups. The only one-symmetry plane in **2** has been reflected by the presence of more signals in the ^1H and ^{13}C NMR spectra: five for protons and six for carbon nuclei. The ^{13}C NMR spectra have proven the presence of sp^2-hybridized carbon atoms in all three compounds **1**−**3** by the appearance of low-field signals within the range of 131−133 ppm.

Comparison of Chemical Behaviors of 1−**3.** The characteristic attribute of compounds **1** and **2** is high chemical inertness of their double bonds. Both compounds do not react with bromine under prolonged contact at ambient temperature or while refluxed in a CCl_4 solution illuminated with a visible light. This is in contrast to **3**, which on treatment with an equimolar amount of bromine in CCl_4 in the dark forms an orange crystalline solid. Microanalysis, though it is not exact enough because of the instability of the material, shows that the solid is a 1:1 adduct **10** of **3** and bromine. The adduct readily loses bromine when dissolved in a polar solvent like methanol, $CHCl_3$, and also $CDCl_3$ and precluded our obtaining its NMR spectra. Adduct **10** essentially resembles the 4,8-di-*tert*-butyl analogue of **3** and bromine reported previously,[8] and therefore, by analogy, polymeric structure **10b** rather than the bromonium bromide **10a** may be assigned to the present adduct. On treatment of **3** with an excess of bromine in $CHCl_3$ at ambient temperature, chromatographically separable di- and tetrabromo derivatives **11** and **12** are formed in a 54% total yield (Scheme 2). The ^1H and ^{13}NMR spectra of **11** are consistent with its symmetrical structure, but the lack of a coupling constant between the two CHBr groups inhibits the assigment of *cis* or *trans* configuration to this compound. The ^1H NMR spectrum is rather complex, but it has been resolved using the COSY technique. The elemental analysis and mass spectrum of **12** are compatible with empirical formula $C_{12}H_{16}Br_4O$, and its structure has been unambiguously established by single-crystal X-ray analysis (Figure 3). Formation of **12** involves an interesting skeletal rearrangement with extrusion of one oxygen atom.

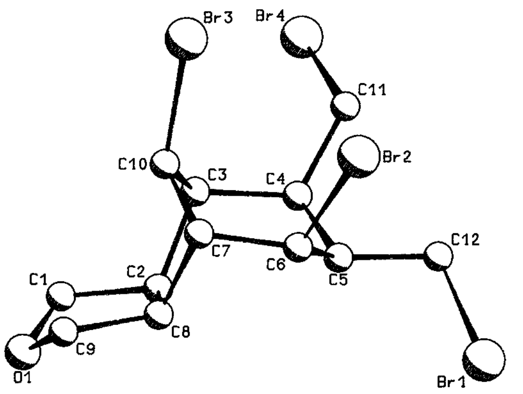
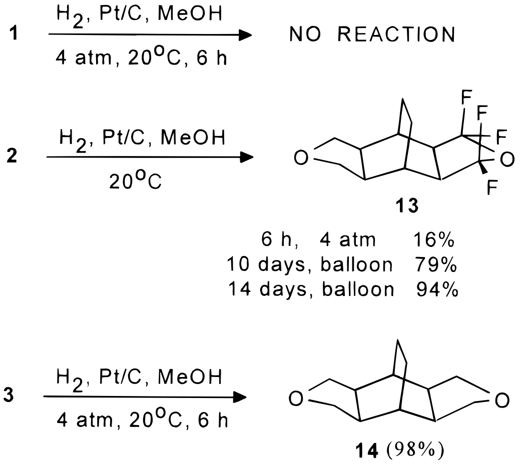


Figure 3. X-ray structure of **12**. Hydrogen atoms are not shown.

Scheme 3



The double bond in octafluoroindacene **1** does not undergo catalytic hydrogenation. Hydrogenation of the one-side fluorinated compound **2** gives its saturated analogue **13**, although the reaction proceeds very slowly; 14 days was required to achieve a 94% conversion. Again, **1** and **2** behave in a different manner than the nonfluorinated indacene **3**, hydrogenation of which proceeds readily to give saturated compound **14** almost quantitatively (Scheme 3).

The attempted oxidations of **1** with *m*-chloroperbenzoic acid and with ozone also failed; in both cases, the starting material was fully recovered. The only successful chemical transformation of **1** was achieved by the use of a strong oxidizing agent such as dimanganese heptaoxide. The conversion was quantitative, and two compounds were formed: the expected oxirane **15** as the minor product and the isomeric compound, internal fluoroacetal **16**, as the major product (Scheme 4). Semiempirical calculations (AM1, MOPAC 6.0 package) have shown that compound **16** is energetically favorable over oxirane **15** by 115.3 kcal/mol.

Compounds **15** and **16** gave the same molecular ion, $m/z = 352$, in their mass spectra but different fragmentation patterns; therefore, they should be considered as structural isomers. The simplicity of the NMR spectrum of **15** indicates a symmetric molecule consistent with the oxirane structure, which has been also confirmed by the lack of OH and CO group absorptions in the IR spectrum of **15**. On the contrary, complexity of the NMR spectra of **16** suggests a highly asymmetric molecule. The ^1H

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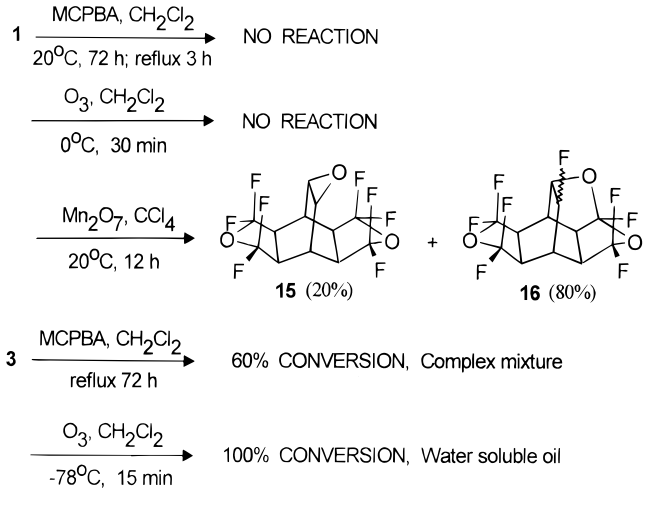
[8] Nakayama, J.; Hirashima, A. *J. Am. Chem. Soc.* **1990**, *112*, 7648.

Scheme 4



NMR spectrum measured at 500 MHz has shown nonequivalence of all bridgehead protons and typical geminal proton-to-fluorine coupling constant (45.8 Hz) for one of the ethylene bridge protons. The ^{19}F NMR spectrum showed three AB systems for the CF_2 groups located at different neighborhoods, one narrow signal for a single fluorine (−O−CF−), and a signal within the range typical for CHF groups (185.6 ppm, $^2J_{HF} = 45.8$ Hz). An interesting spectral feature of compound **16** is large "through-space" coupling ($J_{FF} = 54.3$ Hz) of the CHF group fluorine to a fluorine of one of the CF_2 groups. It has been well documented that pairs of fluorines that are crowded against one another intramolecularly exhibit unusually large nuclear spin−spin coupling constants (45−196 Hz) as measured by ^{19}F NMR spectroscopy.[9] Such F−F coupling has been attributed theoretically to "through-space" nonbonded interactions involving overlap of lone-pair orbitals from the two fluorine atoms.[10] The value of the coupling constant of the CHF group fluorine to the neighboring proton in the ethylene bridge ($^3J_{HF} = 17.8$ Hz) does not allow the determination of their mutual *cis* or *trans* configuration. A literature search led to the conclusion that vicinal fluorine-to-proton coupling constants vary in a broad range of values; this is true for both *cis* and *trans* configurations, and they are strongly dependent on substituents at both carbon atoms.[11] The structure of **16** has also been confirmed by its ^{13}C NMR spectrum; it showed 11 signals, two of them as doublets with geminal C−F coupling constants 242.7 and 187.1 Hz for CFO and CHF, respectively, and two as triplets with $^1J_{CF} = 263.5$ and 262.8 Hz, respectively, for one and two CF_2 groups.

In contrast to **1**, oxidation of nonfluorinated indacene **3** proceeded readily with both *m*-chloroperbenzoic acid and ozone to give complex mixtures of difficult to identify products; IR spectra showed the presence of OH and CO groups.

Conclusions

Fluorinated compounds **1** and **2** constitute a new type of highly unreactive alkenes. It has been found that replacement of CH_2 groups of the tetrahydrofuran rings in nonfluorinated analogue **3** by CF_2 groups dramatically diminishes the reactivity of the ethylene bridge in these compounds. This bridge in **3** behaves like normal alkene, i.e., it readily reacts with bromine and hydrogen and undergoes oxidation while **1** and **2**, in which four or two CH_2 groups have been replaced by CF_2 groups are almost totally inert.

The chemical properties of compunds **1** and **2** resemble that of an analog of **3** substituted at both vinylic positions by bulky *tert*-butyl groups.[8] However, examination of the X-ray structures of both unreactive **1** and reactive **3** do not revealed notable differences in the steric environment of the double bond in these compounds, particularly when the comparable size of hydrogen and fluorine atoms is considered. Therefore, chemical inertness of the ethylene bridge in **1** and **2** could not be explained by steric hindrance created by surrounding fluorine atoms, especially, because in **2** this bridge is flanked by fluorines from one side only.

The lack of reactivity of the double bond in **1** and **2** seems to be a consequence of electronic interactions due the proximity of the double bond-fluorine atoms. The average distance between the ethylene bridge carbon atoms and the neighboring fluorines calculated from the X-ray data of **1** is 2.93 Å, which is closer than the sum of the van der Waals radii of carbon and fluorine atoms (3.05 Å)[7]. This implies an overlap of lone-pair orbitals from fluorine atoms to π-orbitals of the double bond leading to the "through-space" nonbonded interactions. The overlap of the orbitals is facilitated by the fact that the double bond, as found by X-ray analysis, is placed almost in the plane formed by four fluorine atoms (deviation *ca.* 0.5 Å). Such interactions engage the π-orbitals, making them unavailable for external reagents. Somewhat similar "through-space" interactions have been reported for the double bond and proximal aromatic rings in some adducts of anthracene with dienophiles of the norbornene type.[2]

Experimental Section

Anhydride **5** has been prepared according to the previously described procedure.[4] All other starting materials were commercially available reagent-grade chemicals. Melting points were determined in capillaries and are uncorrected. Elemental analyses for C and H were performed by the analytical laboratory using standard procedures. The halogens were determined by a Rowley and Churchill method[12] after combustion of samples under an atmosphere of oxygen in a Schöniger flask.[13] ^{1}H, ^{19}F, and ^{13}C NMR spectra were recorded in $CDCl_3$ or in other solvents, as indicated, at 200 or 500, 188, and 50 MHz, respectively. Chemical shifts are quoted in ppm relative to internal TMS for protons and carbon nuclei and relative to internal $CFCl_3$ for fluorine nuclei. GC−MS analyses were performed using a 30 m capillary column coated with an HP5 oil.

Crystal Structure Analysis of 1, 3, and 12. Well-shaped crystals were chosen for X-ray diffraction investigations.[19] The stability of the crystals was controlled on three reflections at 50 reflection intervals. Lorentz and polarization corrections were applied to all data. In the case of **12**, the absorption correction was performed.

The phase problem was solved by direct methods using the SHELXS-86 program,[14] which revealed the following information on E-maps: in the case of **1**, the positions of all nonhydrogen atoms; in the case of **3**, in addition to all expected

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(9) Mallory, F. B.; Mallory, C. W.; Ricker, W. M. *J. Org. Chem.* **1985**, *50*, 457 and references therein.

(10) Mallory, F. B. *J. Am. Chem. Soc.* **1973**, *95*, 7747.

(11) (a) Emsley, J. W.; Phillips, L.; Wray, V. *Fluorine Coupling Constants*; Pergamon Press: Oxford, 1977. (b) Webb. G. A. *Annual Reports on NMR Spectroscopy*; Academic Press: London, 1983, Vol. 14.

(12) Rowley, R. J.; Churchill, H. V. *Ind. Eng. Chem. Anal. Ed.* **1937**, *9*, 551.

(13) (a) Schöniger, W. *Microchem. Acta* **1955**, 123. (b) Małysz, D. *Acta Pol. Pharm.* **1968**, *3*, 275.

atomic positions, some additional electron peaks that may point to a positional disorder in the structure; and in the case of **12**, four bromine positions. Therefore, a conclusion was drawn that in molecule **3** a positional disorder of some atoms is present. As a matter of fact, peaks on the E-map revealed two molecules of **3** superimposed one on another with a common C−O−C fragment of one of the furan rings, common C-2 and C-12 atoms of the other furan ring, and common bridgehead atoms C-4 and C-10 (Figure 2). The rest of the non-hydrogen atomic positions in **12** were found from difference E-maps after isotropic refinement of bromine atoms.

Full-matrix least-square refinements of positional and thermal parameters were done by the same method for the three structures in question (SHELXL-93 program[15]). For disordered atoms in **3** a site occupation ratio of 1:1 was set invariantly. Both structures were initially refined in isotropic and then in anisotropic mode. For **12** the result was not satisfactory ($R > 0.09$), possibly due to multiple reflection of the beam in the crystal ($D_x = 2.30$). To correct this effect, program DIFABS[16] was used working on the set of atomic parameters of isotropic approximation. Positional parameters of hydrogen atoms were set from geometrical calculations and refined as “riding” on their adjacent carbon atoms. The final refinement results have been deposited with the Cambridge Crystallographic Data Centre.[19]

***exo,exo*-4,8-Etheno-1,1,3,3,5,5,7,7-octafluoro-2,6-dioxaperhydro-*s*-indacene (1).** Anhydride **5** (1.1 g, 3.7 mmol) and water (0.08 mL, 4.3 mmol, equivalent of 8.6 mmol of HF generated in the reaction with SF_4) were placed in a 30 mL capacity stainless steel autoclave and then, after the mixture was cooled *ca.* −78 °C (dry ice−acetone bath), the autoclave was evacuated to *ca.* 2 Torr and sulfur tetrafluoride (3.5 g, 3.2 mmol) was condensed into it. The charged autoclave was heated in a rocking muffle at 85 °C for 48 h, after which time it was allowed to cool to ambient temperature and the gaseous products (SOF_2, HF, excess SF_4) were let off. A solid residue was vacuum sublimed (180 °C, 0.5 Torr) and recrystallized from toluene to give **1** (0.8 g, 64%) as colorless prisms: mp 224−225 °C; ^{1}H NMR (acetone-d_6) δ 3.52 (complex m, 6H), 6.29 (narrow m, 2H, vinylic); ^{19}F NMR (acetone-d_6) δ −53.6 and −77.1 (AB system, dm, $^2J = 146.7$ Hz, 8F); ^{13}C NMR (acetonitrile-d_3) δ 30.2 (qn, $^3J_{CF} = 4.2$ Hz, bridgehead), 47.7 (dd, $^2J_{CF} = 31.5$, 21.2 Hz), 128.8 (td, $^1J_{CF} = 261.0$ Hz, $^3J_{CF} = 7.8$ Hz, CF_2), 131.0 (s, vinylic); GC−MS *m/z* (rel intensity) 336 (M$^+$, 35), 194 ($C_8H_6F_4O^+$, 100), 128 ($C_7H_4F_2^+$, 80). Anal. Calcd for $C_{12}H_8F_8O_2$: C, 42.87; H, 2.40; F, 45.21. Found: C, 42.87; H, 2.38; F, 45.19.

Dimethyl 3,3,5,5-Tetrafluoro-4-oxatricyclo[5.2.2.0^{2,6}]undec-10-ene-8,9-dicarboxylate (6). Anhydride **5** (4 g, 13.5 mmol), methanol (15 mL), and a few drops of concentrated sulfuric acid were refluxed for 12 h. After evaporation of the solution to *ca.* 1/3 of its initial volume, water was added (20 mL) and organic material was extracted with ether (3 × 10 mL). The combined extracts were dried over anhydrous $MgSO_4$, and the solvent was removed under reduced pressure. The remaining solid was recrystallized from methanol to give **6** (3.7 g, 81%) as long needles: mp 166−168 °C. ^{1}H NMR ($CDCl_3$) δ 3.00 (s, 2H), 3.10 (complex m, 2H), 3.37 (broad s, 2H), 3.64 (s, 6H, CH_3), 6.35 (m, 2H, vinylic); ^{19}F NMR ($CDCl_3$) δ −54.2 and −78.4 (AB system, dm, $^2J = 146.3$ Hz, 4F); ^{13}C NMR ($CDCl_3$) δ 32.2 (t, $^3J_{CF} = 4.0$ Hz, bridgehead), 44.9 (s), 48.3 (dd, $^2J_{CF} = 31.8$, 22.2 Hz), 52.0 (s, CH_3), 128.4 (td, $^1J_{CF} = 262.0$ Hz, $^3J_{CF} = 8.0$ Hz, CF_2), 130.0 (s, vinylic), 171.5 (s, CO); GC−MS *m/z* (rel intensity) 338 (M$^+$, 55), 307 (M$^+$ − MeO, 100), 279 (M$^+$ − $C0_2Me$, 90), 259 (M$^+$ − CO_2Me − HF, 55), 194 ($C_8H_6F_4O^+$, 40), 128 ($C_7H_6F_2^+$, 80); IR (KBr) 1739 cm^{-1}. Anal. Calcd for $C_{14}H_{14}F_4O_5$: C, 49.71; H, 4.17; F, 22.47. Found: C, 49.60; H, 4.15; F, 22.50.

3,3,5,5-Tetrafluoro-8,9-bis(hydroxymethyl)-4-oxatricyclo[5.2.2.0^{2,6}]undec-10-ene (7). A solution of diester **6** (3 g, 9 mmol) in anhydrous THF (20 mL) was added dropwise at ambient temperature to a stirred suspension of $LiAlH_4$ (3 g, 79 mmol) in THF (150 mL) under an atmosphere of dry argon. The mixture was stirred for 12 h, and then, while the mixture was vigorously stirred, water was added in such an amount to hydrolize an excess of the reagent. The mixture was left until a white precipitate of metal hydroxides sedimentated, a clear solution was separated, the solid was washed with THF (2 × 50 mL), and the combined solutions were dried over $MgSO_4$. Removal of the solvents gave crude diol **7** (1.8 g, 6.38 mmol) as an oily liquid: GC−MS *m/z* (rel intensity) 282 (M$^+$, 7), 264 (M$^+$ − H_2O, 10), 252 (M$^+$ − CH_2O, 15), 194 ($C_8H_6F_4O^+$, 45), 127 ($C_7H_4F_2^+$, 100). The diol was used for the next step without purification.

***exo,exo*-4,8-Etheno-1,1,3,3-tetrafluoro-2,6-dioxaperhydroindacene (2).** The crude diol **7** (1.8 g, 6.38 mmol) and $KHSO_4$ (6 g, 44 mmol) were ground together, placed in an open glass tube, and heated gradually on an oil bath to 220 °C and then kept at this temperature for 2 h. The product sublimed and condensed in the upper part of the tube. The sublimate was recrystallized from methanol to give **2** as white crystals (0.6 g, 36%): mp 132−134 °C; ^{1}H NMR ($CDCl_3$) δ 2.45 (m, 2H), 3.06 (m, 4H), 3.43 (m, 2H), 3.88 (m, 2H), 6.24 (m, 2H, vinylic); ^{19}F NMR ($CDCl_3$) δ -53.4 and −76.9 (AB system, dm, $^2J = 146.2$ Hz, 4F); ^{13}C NMR ($CDCl_3$) δ 32.3 (t, $^3J_{CF} = 3.8$ Hz, bridgehead), 42.9 (s), 48.9 (dd, $^2J_{CF} = 30.2$, 22.3 Hz), 71.9 (s) 128.4 (dt, $^1J_{CF} = 261.6$ Hz, $^3J_{CF} = 8.2$ Hz, CF_2), 131.3 (s, vinylic); GC−MS *m/z* (rel intensity) 264 (M$^+$, 10), 194 ($C_8H_6F_4O^+$, 5), 127 ($C_7H_5F_2^+$, 30), 69 ($C_4H_5O^+$, 100). Anal. Calcd for $C_{12}H_{12}F_4O_2$: C, 54.55; H, 4.58; F, 28.76. Found: C, 54.37; H, 4.72; F, 28.51.

Tetramethyl Bicyclo[2.2.2]oct-7-ene-*exo*-2,3,5,6-tetracarboxylate (8). Tetraester **8** was obtained by following the procedure described for its tetraethyl analogue:[17] yield 95%; mp 130−132 °C (lit.[6] mp 132−133 °C); ^{1}H NMR ($CDCl_3$) δ 3.08 (s, 4H), 3.34 (narrow m, 2H, bridgehead), 3.62 (s, 12 H, CH_3O), 6.41 (m, 2H, vinylic).

***exo*-2,3,5,6-Tetrakis(hydroxymethyl)bicyclo[2.2.2]oct-7-ene (9).** Tetraol **9** was obtained by following the literature procedure:[18] yield 82%; mp 179−181 °C (lit.[18] mp 180−181 °C).

***exo,exo*-4,8-Etheno-2,6-dioxaperhydro-*s*-indacene (3).** Tetraol **9** (0.9 g, 4 mmol) and $KHSO_4$ (4 g, 29 mmol) were ground together, placed in an open glass tube, and heated gradually in an oil bath to 220 °C and then kept at this temperature for 1 h. The product sublimed and condensed in the upper part of the tube. The total contents of the tube were ground and washed with $CHCl_3$ (3 × 10 mL). The combined eluents were evaporated, and a dark residue was vacuum sublimed (100 °C/20 Torr) to give **3** as colorless crystals (0.34 g, 44%). An analytical sample was obtained by recrystallization from methanol: mp 124−125 °C (lit. 206−207 °C[6]); ^{1}H NMR ($CDCl_3$) δ 2.51 (m, 4H), 2.64 (m, 2H, bridgehead), 3.83 and 3.39 (two AB systems, 8H), 6.23 (m, 2H vinylic); ^{13}C NMR ($CDCl_3$) δ 35.9 (s, bridgehead), 45.2 (s), 72.3 (s, CH_2), 133.3 (s, vinylic); GC−MS *m/z* (rel intensity) 192 (M$^+$, 20), 122 ($C_8H_{12}O^+$, 40), 91 ($C_7H_7^+$, 100), 69 ($C_4H_5O^+$, 75). The product was contaminated with 7% of the *exo,endo* isomer: *m/z* 192, 162 (M$^+$ − CH_2O, 100), 91, 69. Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.97; H, 8.39. Found: C, 74.74; H, 8.34.

Attempted Bromination of 1 and 2. Solutions of compounds **1** or **2** (100 mg, 0.3−0.4 mmol) and bromine (500 mg, 3 mmol) in CCl_4 or CH_2Cl_2 (5 mL) were placed in a Pyrex glass tube and refluxed and illuminated with a 100-W visible light lamp for 24 h. The solvent and bromine were removed under reduced pressure, and the residues were subjected to GC−MS investigations; no product other than the starting material was detected.

Bromination of 3 with 1 Equiv of Bromine. A solution of bromine (90 mg, 0.56 mmol) in CCl_4 (4 mL) was added to a solution of alkene **3** (100 mg, 0.52 mmol) in CCl_4 (2 mL) at 0 °C. An orange precipitate formed immediately. After the mixture was stirred overnight in the dark, the precipitate was filtered off, washed with a small amount CCl_4, and dried for 3 days in air at room temperature to give adduct **10** (80 mg, 44%). Anal. Calcd for $C_{12}H_{16}Br_2O_2$: Br, 45.4. Found: Br,

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47.2. ^{1}H NMR ($CDCl_3$) spectrum was indentical with the spectrum of **3**. GLC analyses of solutions of the adduct **10** in methanol or $CHCl_3$ revealed only compound **3**.

Bromination of 3 with an Excess of Bromine. Bromine (4 g, 25 mmol) was added to a solution of **3** (1.1 g, 5.7 mmol) in CH_2Cl_2 (5 mL) at −78 °C. An orange precipitate formed immediately. The reaction mixture was stirred overnight at room temperature, and then the solvent and an excess of bromine were removed under vacuum to give a dark-red oil (2.6 g). Column chromatography on silica gel using CH_2Cl_2 as an eluent gave compounds **11** (660 mg, 33%) and **12** (600 mg, 21%) and an unidentified tar (1.2 g).

***exo,exo*-4,8-(1,2-Dibromoethano)-2,6-dioxaperhydro-*s*-indacene (11):** mp 197−200 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.37−2.46 (broad m, 6H), 3.53 and 4.75 (AB system, ^2J = 9.6 Hz, 4H, CH_2), 3.74 and 3.98 (AB system, ^2J = 10.0 Hz, 4H, CH_2), 4.72 (s, 2H, CHBr), coupling constants were obtained using the decoupling technique; ^{13}C NMR (200 MHz, $CDCl_3$) δ 40.4, 41.7, 44.3, 52.4 (CHBr), 69.8 and 71.5 (CH_2O); GC−MS *m/z* (rel intensity) 350 [M^+ (2 × ^{81}Br), 3], 271 [M^+ − Br (^{81}Br), 15], 191 (M^+ − HBr, 100). Anal. Calcd for $C_{12}H_{16}Br_2O_2$: C, 40.94; H, 4.58; Br, 45.39. Found: C, 40.82; H, 4.60; Br, 45.67.

8,9-Bis(bromomethyl)-10,11-dibromo-4-oxatricyclo-[5.3.1.0^{2,6}]undecane (12): mp 161−163 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.37−2.45 (complex m, 2H), 2.48−2.60 (complex m, 2H), 2.81 (t, ^3J = 3.6 Hz, 1H, C*H*CH_2Br), 2.88 (t, ^3J = 3.4 Hz, 1H, C*H*CH_2Br), 3.58−3.74 (complex m, 5H), 3.90 (complex, 2H), 4.45 (m, 3H); assignments of signals based on COSY technique; ^{13}C NMR (200 Mz, $CDCl_3$) δ 32.6, 35.7, 40.3, 41.1, 45.0, 45.5, 47.1, 47.3, 50.1, 73.6 (CH_2O); 74.2 (CH_2O), MS *m/z* (all ^{81}Br ions, relative intensity) 492 (M^+, <1), 413 (M^+ − Br, 25), 383 ($C_{11}H_{14}Br_3^+$, 5), 333 (M^+ − HBr_2, 50), 303 ($C_{11}H_{13}Br_2^+$, 25), 252 (M^+ − H_2Br_3, 35), 223 ($C_{11}H_{12}Br^+$, 35), 143 ($C_5H_4Br^+$, 45). Anal. Calcd for $C_{12}H_{16}Br_4O$: C, 29.07; H, 3.25; Br, 64.46. Found: C, 28.90; H, 3.30; Br, 64.76. The structure of compound **12** was confirmed by X-ray crystallography (Figure 3).

Attempted Hydrogenation of 1. A solution of compound **1** (100 mg, 3 mmol) in methanol (20 mL) containing palladium catalyst (10% Pt/C, 0.5 g) was placed in a Parr apparatus and hydrogenated (4 atm H_2) at ambient temperature for 6 h. GC−MS analysis showed only unreacted **1**.

Hydrogenation of 2. A solution of compound **2** (20 mg, 0.075 mmol) in methanol (20 mL) containing palladium catalyst (10% Pd/C, 100 mg) was hydrogenated in a Parr apparatus at ambient temperature. The reaction was monitored by GC−MS. The conversion was 16% after 6 h (4 atm H_2), 79% after 10 days, and 94% after 14 days (*ca.* 0.3 atm H_2, from a balloon). The catalyst was filtered off, and the solution was evaporated to give a solid (20 mg), which after recrystallization from methanol afforded pure compound **13** as white crystals.

***exo,exo*-4,8-Ethano-1,1,3,3-tetrafluoro-2,6-dioxaperhydroindacene (13):** mp 128−130 °C; ^{1}H NMR ($CDCl_3$) δ 1.66 (s, 4H, CH_2CH_2), 2.03 (s, 2H, bridgehead), 2.24 (m, 2H), 2.85 (m, 2H), 3.70 and 3.95 (AB system, $^2J_{AB}$ = 10.3 Hz, 4H, CH_2O); ^{19}F NMR ($CDCl_3$) δ −50.5 and −82.7 (AB system, dm, $^2J_{FF}$ = 149.3 Hz, CF_2); ^{13}C NMR ($CDCl_3$) δ 13.9 (d, $^4J_{CF}$ = 4.7 Hz, CH_2), 27.3 (d, $^3J_{CF}$ = 4.3 Hz, bridgehead), 39.7 (s), 45.7 (dd, $^2J_{CF}$ = 30.6, 21.4 Hz), 71.5 (s), 129.6 (td, $^1J_{CF}$ = 266.0 Hz, $^3J_{CF}$ = 9.5 Hz); GC−MS m/z (rel intensity) 266 (M^+, 100), 194 ($C_8H_6F_4O^+$, 85), 127 ($C_7H_5F_2^+$, 80); HRMS calcd for $C_{12}H_{14}F_4O_2$ M^+ 266.09299, found 266.093311.

Hydrogenation of 3. A solution of compound **3** (200 mg, 1 mmol) in methanol (20 mL) containing palladium catalyst (10% Pd/C, 100 mg) was hydrogenated (4 atm H_2) in a Parr apparatus at ambient temperature for 6 h. The catalyst was filtered off, and the solution was evaporated to give a solid that was vacuum sublimed (100 °C/1 Torr) and then recrystallized from CCl_4/*n*-pentane (1:1) to give pure compound **14** (200 mg, 98%) as white crystals.

***exo,exo*-4,8-Ethano-2,6-dioxaperhydro-*s*-indacene (14):** mp 120−122 °C (lit.[20] mp 122 °C); ^{1}H NMR ($CDCl_3$) δ 1.52 (s, 4H, CH_2CH_2), 1.54 (s, 2H, bridgehead), 2.28 (narrow m, 4H), 3.69 and 3.90 (AB system, $^2J_{AB}$ = 8.8 Hz, 8H, CH_2O); GC−MS *m/z* (rel intensity) 194 (M^+, 20), 122 ($C_8H_{10}O^+$, 30), 105 ($C_8H_9^+$, 55), 79 ($C_6H_7^+$, 100), 69 ($C_4H_5O^+$, 80), 41 ($C_3H_5^+$, 98), 28 ($C_2H_4^+$, 95). Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.19; H, 9.29.

Attempted Oxidation of 1 with *m*-CPBA. A solution of **1** (100 mg, 0.3 mmol) and *m*-chloroperbenzoic acid (100 mg, 0.6 mmol) in CH_2Cl_2 (10 mL) was stirred for 3 days at ambient temperature and then refluxed for 2 h. The acid was washed out with an aqueous solution of $NaHCO_3$, dried over $MgSO_4$, and subjected to GC−MS analysis: no other compound but starting **1** was detected.

Attempted Ozonolysis of 1. A solution of **1** (0.5 g, 1.5 mmol) in CH_2Cl_2 (500 mL) was treated with ozone at 0 °C for 30 min. The solvent was partially removed under vacuum, and the remaing solution was stirred in 30% H_2O_2 (5 mL) at ambient temperature for 24 h. The organic layer was separated and dried over $MgSO_4$. Evaporation of the solvent gave a solid (0.5 g) that by GC−MS was identified as the starting material.

Oxidation of 1 with Mn_2O_7. A solution of Mn_2O_7 (10 g, 45 mmol) in CCl_4 (100 mL) was poured into a vigorously stirred solution of **1** (0.7 g, 2 mmol) in CCl_4 (700 mL) at ambient temperature. The solution was left for 12 h, and then a 50% aqueous solution of glyoxylic acid was added until manganese salts fully precipitated. The solid was filtered off, and the solution was evaporated to give a solid (0.7 g) that was found by GC−MS and NMR analyses to consist of compounds **15** (20%) and **16** (80%). Anal. Calcd for $C_{12}H_8F_8O_3$: C, 40.93; H, 2.29; F, 43.16. Found: C, 40.92; H, 2.25; F, 43.38.

***exo,exo*-4,8-Epoxyethano-1,1,3,3,5,5,7,7-octafluoro-2,6-dioxaperhydro-*s*-indacene (15):** ^{19}F NMR ($CDCl_3$) δ −50.3 and −74.3 (AB system, $^2J_{FF}$ = 145.6 Hz, CF_2), −54.8 and −76.1 (AB system, $^2J_{FF}$ = 152.4 Hz); GC−MS *m/z* (rel intensity) 352 (M^+, 60), 332 (M^+ − HF, 20), 305 (M^+ − COF, 40), 257 ($C_{10}H_7F_6O^+$, 20), 146 ($C_7H_5F_3^+$, 100), 127 ($C_7H_5F_2^+$, 50), 95 ($C_6H_4F^+$, 60).

3,5,5,9,9,11,11,14-Octafluoro-4,10,15-trioxapentacyclo[5.5.2.1^{3,13}.0^{2,6}.0^{8,12}]pentadecane (16): ^{1}H NMR (500 MHz, acetone-*d*$_6$) δ 3.08 (m, 2H, $CHCF_2$), 3.20 (s, 1H, bridgehead), 3.25 (narrow m, 1H, bridgehead), 3.35 (m, 1H, $CHCF_2$), 3.61 (dddd, $^3J_{HF}$ = 14.6 Hz, *J* = 11.6, 7.0, 4.5 Hz, 1H, $CHCF_2$), 4.73 (dt, $^3J_{HF}$ = 17.8 Hz, $^3J_{HH}$ = ca. 4.5 Hz, 1H, CHO), 4.86 (dd, $^2J_{HF}$ = 45.8 Hz, $^3J_{HH}$ = ca. 4.5 Hz, 1H, CHF); ^{19}F NMR (200 Mz, acetone-*d*$_6$) δ 49.8 and 72.2 (AB system, $^2J_{FF}$ = 148.2 Hz, CF_2), 53.7 and 82.0 (AB system, $^2J_{FF}$ = 148 Hz, CF_2; the higher field signal appears as dd, $^5J_{FF}$ = 54.3 Hz), 56.8 and 77.2 (AB system, $^2J_{FF}$ = 151.0 Hz, CF_2), 85.5 (sharp m, CF), 185.6 (ddd, $^5J_{FF}$ = 54.3 Hz, $^2J_{HF}$ = 45.8 Hz, $^3J_{HF}$ = 17.8 Hz, CHF); ^{13}C NMR (acetonitrile-*d*$_6$) δ 29.9 (m, bridgehead), 33.8 (s, bridgehead), 40.1 (dd, $^2J_{CF}$ = 23.6 and 34 Hz, *C*CF_2), 43.8 (dd, $^2J_{CF}$ = 23.6, 37.2 Hz, *C*CF_2), 44.7 (d, $^2J_{CF}$ = 22.8 Hz, *C*CFO), 46.1 (dd, $^2J_{CF}$ = 23.9, 33.0 Hz, *C*CF_2), 79.8 (ddd, $^2J_{CF}$ = 31.9 Hz, $^3J_{CF}$ = 7.6, 2.5 Hz, CHO), 88.9 (ddd, $^1J_{CF}$ = 187 Hz, $^4J_{CF}$ = 4.8, 1.8 Hz, CHF), 129.8 (tm, $^1J_{CF}$ = ca. 263 Hz, 2 CF_2), 130.4 (td, $^1J_{CF}$ = 263.5 Hz, $^3J_{CF}$ = 7.9 Hz, *C*F_2OCFO), 134.2 (ddd, $^1J_{CF}$ = 242.7 Hz, $^3J_{CF}$ = 4.6, 2.5 Hz, CFO); GC−MS *m/z* (rel intensity) 352 (M^+, 15), 288 (M^+ − CO_2 − HF, 100), 212 ($C_8H_5F_5O^+$, 45), 145 ($C_7H_4F_3^+$, 55), 95 ($C_6H_4F^+$, 50).

Oxidation of 3 with *m*-CPBA. A solution of **3** (250 mg, 1.3 mmol) and *m*-chloroperbenzoic acid (1 g, 6 mmol) in CH_2Cl_2 (50 mL) was refluxed for 3 days. The solution was washed with an aqueous solution of $NaHCO_3$ and dried over $MgSO_4$. Removal of the solvent gave a solid (0.23 g) that was found by GC−MS analysis to consist of unreacted **3** (ca. 40%), five compounds with molecular peaks *m/z* = 208, and one compound with molecular peak *m/z* = 206 (23%).

Ozonolysis of 3. A solution of **3** (0.25 g, 1.3 mmol) in CH_2Cl_2 (75 mL) was treated with ozone at −78 °C for 15 min, and then the solution was stirred in 30% H_2O_2 (5 mL) at ambient temperature for 20 h. The organic layer was separated and dried over $MgSO_4$. Evaporation of the solvent gave a water-soluble oil (0.2 g): IR (film) 2500−3600 cm^{-1} (broad, OH), 1752 and 1735 cm^{-1} (strong, CO). No unreacted **3** was found.

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