

Thermal Isomerization of Perfluorobicyclo[2.2.0]hexene Oxides¹

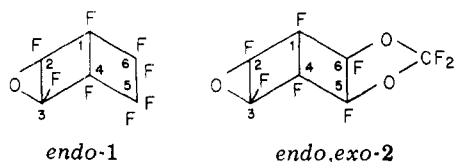
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Due to a continuing interest in the area of new perfluoropolymer forming reactions, we investigated the reaction of para-bonded hexafluorobenzene² and bis-(fluoroxy)difluoromethane.³ During the course of the study, we found that $\text{CF}_2(\text{OF})_2$ decomposed under photolysis into intermediates in the presence of $\text{C}=\text{C}$ bonds at -40°C in an inert perfluoropentane solvent. The suggested active intermediates are fluorine atoms, $\cdot\text{OCF}_2\text{O}\cdot$ diradicals, fluoroxy radicals, and oxygen atoms in the presence of carbonyl fluoride, which was detected by IR in the gas phase. When the oxygen atom and fluorine atoms or $\cdot\text{OCF}_2\text{O}\cdot$ diradical were added to the para-bonded hexafluorobenzene, perfluorobicyclo[2.2.0]hexane oxides were formed.

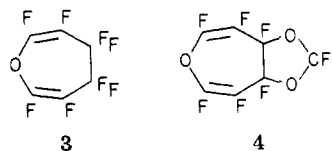
Since the perfluorinated epoxides such as hexafluoropropylene oxide and tetrafluoroethylene oxide have received significant attention, we report 2,3-epoxyoctafluorobicyclo[2.2.0]hexane (1) and 2,3-epoxy-5,6-(di-



fluoromethylenedioxy)hexafluorobicyclo[2.2.0]hexane (2). Compound 1 is an adduct of perfluorobicyclo[2.2.0]hexa-2,5-diene with one oxygen atom and two fluorine atoms, while compound 2 is an adduct with one $\cdot\text{OCF}_2\text{O}\cdot$ diradical and one oxygen atom. Their structural conformations were elucidated by ¹⁹F NMR (Table I) as *endo*-1 and *endo,exo*-2. The assignments were assisted by the previously reported hexafluorobicyclo[2.2.0]hexanes and -hexenes.^{4,5} The assignment of the *endo* fluorines downfield from the *exo* fluorines is in agreement with Barlow et al.⁴ In Table I, the compounds containing the tertiary *endo* fluorines show absorptions in the range of 111–130 ppm and the bridgehead fluorines in the range of 197–200 ppm. The literature values of the bridgehead fluorines of octafluorobicyclo[2.2.0]hex-2-ene and "Dewar" C_6F_6 were 199.9 and 191.0 ppm, respectively.^{6,7} The difluoromethylenedioxy groups are an AB type and show absorption about 56 ppm for the *endo* fluorines and in the range of 61–64 ppm for the *exo* fluorines. Our previously reported values of OCF_2O groups in 1,2-(difluoromethylenedioxy)perfluorocyclohex-3-ene and -hexa-3,5-

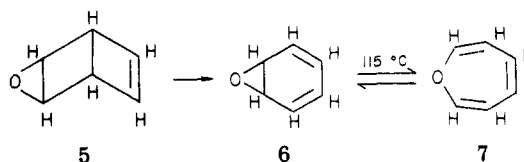
diene were in the range of 52–58 and 61–63 ppm.⁸ The assignments of the *J* values were confirmed by the ¹⁹F-decoupling techniques and computer programs.^{8,9}

The decreasing IR absorbance at 1545 cm^{-1} (i.e., the epoxide group of 1 and 2) was observed with respect to time with a new absorbance increasing at 1750 cm^{-1} (i.e., the olefinic bonds of 3 and 4, respectively). The semilog



plots of the absorbances ($A_0 - A$ at 1750 cm^{-1}) for 3 and 4 and (A at 1545 cm^{-1}) for 1 and 2 vs. time follow a first-order dependence over several half-lives. The half-life at 160°C of 1 to 3 was 3.8 min and that of 2 to 4 was 6.7 min.

Although the rearrangement of the monoxide (5) was



previously reported^{10,11} to form benzene oxide (6) undergoing rapid thermal equilibrium with oxepin (7) at 115°C , the thermal isomerization of 1 and 2 to 1,6-epoxyoctafluorohexa-1,5-diene (3) and 3,4-(difluoromethylenedioxy)-1,6-epoxyhexafluorohexa-1,5-diene (4), respectively, was a single-step irreversible conversion.

Experimental Section

Preparation of Perfluorobicyclo[2.2.0]hexene Oxides (1 and 2). In a typical run, $\text{CF}_2(\text{OF})_2$ (7–20 mmol) was slowly added by increments for a period of 1–3 h under photolysis and vacuum manipulation to a solution containing an equal molar ratio of "Dewar" C_6F_6 (90–95% in hexafluorobenzene in $n\text{-C}_5\text{F}_{12}$ solvent in a quartz reaction vessel. The quartz vessel was maintained at -40°C by an alcohol coolant bath in a quartz Dewar flask. A 200-W high-pressure mercury arc lamp was utilized as an outside irradiation source for a period of 2 h.

The product mixtures were evacuated at -196°C for the noncondensable gas and were progressively warmed from -196 to -25°C for removing the traces of the decomposition products such as COF_2 and mainly $n\text{-C}_5\text{F}_{12}$ solvent. The distillate was periodically monitored by infrared analyses. The distillate which collected in the liquid nitrogen trap between -25 and 25°C , till the vapor pressure reached less than 1 mm Hg at 25°C , was the volatile fraction. The volatile fraction (about 40% yield) was subsequently fractionated by gas chromatography into five perfluorobicyclo[2.2.0]hexane derivatives. A stainless steel column filled with OV-210 on Chromosorb W at 80°C was used with 15-atm helium as the carrier gas. The two perfluorobicyclo[2.2.0]hexene oxides (1 and 2) at about 2 and 6% yield, respectively, were isolated as the second and fourth fractions from the volatile products.

A GC-IR analyzer (Perkin-Elmer Model 567 and Sadtler CIRA

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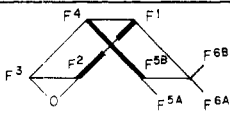
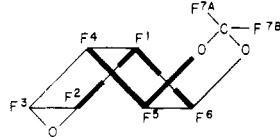
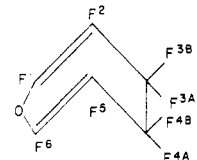
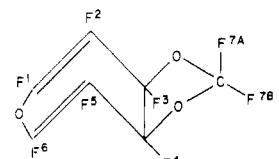
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Table I. ^{19}F NMR of Some Perfluorobicyclohexene Oxides and Their Isomers

compd	formula	assign	chem shift ^a (ppm from CFCl_3)	J , Hz ± 1
1		F(2,3) exo F(5A,6A) endo F(5B,6B) exo F(1,4)	181.6 117.5 135.0 199.5	$J(5A,5B) = J(6A,6B) = 234$; $J(1,2) = J(1,3) = J(1,5A) = J(1,6B) = J(2,4) = J(3,4) = J(4,5B) = J(4,6A) = J(4,6B) = 9$
2		F(7A) endo F(7B) exo F(2,3) exo F(5,6) endo F(1,4)	56.0 63.9 181.5 129.6 197.6	$J(7A,7B) = 67.3$; $J(7B,6) = J(7B,5) = 5.5$; $J(1,2) = J(3,4) = 12$; $J(3,5) = J(2,6) = 8$; $J(1,6) = J(4,5) = 12$
3		F(1,6) F(3A,4A) endo F(3B,4B) exo F(2,5)	96.3 118.3 ^b 118.3 ^b 181.3	$J(1,2) = J(5,6) = 26$
4		F(7A) endo F(7B) exo F(1,6) F(3,4) endo F(2,5)	56.1 61.8 93.3 111.2 176.9	$J(7A,7B) = 71.0$; $J(7B,3) = J(7B,4) = 8.9$; $J(1,2) = J(5,6) = 30$; $J(1,3) = J(4,6) = 12$; $J(2,3) = J(4,5) = 23$

^a Parts per million from CFCl_3 . ^b Collapsed AA'BB' system.

101) was used to record the IR absorptions. The detector was set at 180 °C, the IR cell was maintained at 162 °C (which was measured with a thermocouple), and the injection port was at 160 °C.

The GC/MS (LKB9000 at 13 eV) of the unisomerized molecules 1 and 2 showed m/e values of parent ions at 240 ($\text{C}_6\text{F}_8\text{O}^+$) for 1 and at m/e 284 ($\text{C}_7\text{F}_8\text{O}_3^+$) for 2. After the sample was heated at 190 °C for 45 min, the GC/MS data recorded two identical m/e values of parent ions m/e at 240 ($\text{C}_6\text{F}_8\text{O}^+$) and 284 ($\text{C}_7\text{F}_8\text{O}_3^+$) but with different elution times and mass cracking patterns indicating the presence of isomers 3 for the former and 4 for the latter.

Mass spectroscopic molecular weight (CEC21-110-B) of 3:

Calculated for $\text{C}_6\text{F}_8\text{O}$: 239.9821. Found: 239.9814.

Mass spectroscopic molecular weight (CEC21-110-B) of 4:
Calculated for $\text{C}_7\text{F}_8\text{O}_3$: 283.9720. Found: 283.9721.

Acknowledgments. We thank the Air Force Office of Scientific Research for support under Contract F44620-76-C-0027, Dr. D. Thomas for mass spectra, and Mr. L. Cary for ^{19}F NMR.

Registry No. 1, 69655-83-0; 2, 69655-85-2; 3, 69655-87-4; 4, 70428-88-5; $\text{CF}_2(\text{OF})_2$, 16282-67-0; Dewar C_6F_6 , 6733-01-3.

Communications

Evidence for the Formation of a Symmetrical Ion during Neighboring Group Participation by the Cyclopropyl Moiety. Solvolysis of Methylated Derivatives of Tricyclo[3.2.1.0^{2,4}]octan-8-ol

Summary: Solvolysis of methylated derivatives of tricyclo[3.2.1.0^{2,4}]octan-8-ol *p*-nitrobenzoate esters gave products which were only consistent with the intermediacy of highly delocalized nonclassical ions.

Sir: The dialogue concerning the nature of certain types of carbocations generated in solvolysis reactions has been a long and vigorous one.¹ Among those systems, for which the nature of neighboring group participation has been

questioned,² is tricyclo[3.2.1.0^{2,4}]octan-8-ol.^{3,4} The basic question which required answering was whether 1 ionized to produce the rapidly equilibrating pair of ions represented by the mirror image structures 2 and 3, or whether the trishomocyclopropenyl cation, 4, was the crucial intermediate. Some time ago we demonstrated that methyl substitution on the participating function could be used to establish the symmetrical nature of the participation

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(4) The existence of neighboring group participation by the cyclopropyl moiety of this system is supported by the 10¹⁴ rate difference between this system and the 7-bicyclo[2.2.1]heptyl system. Thus, the existence of neighboring group participation has not been questioned. Only the nature of the transition state and the structure of the cationic intermediate have been debated.

(1) For a recent summation of one point of view see H. C. Brown, "The Nonclassical Ion Problem", Plenum Press, New York, N.Y., 1977.

(2) Reference 1, p 273.