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SOME NEW PERFLUOROETHERS AND COPOLYMERS FROM 'DEWAR' HEXAFLUOROBENZENE

M.S. TOY and R.S. STRINGHAM, Science Applications, Inc., 1257 Tasman Drive
Sunnyvale, California 94086

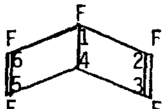
SUMMARY

The thermal and photolytic reactions of hexafluorobicyclo[2.2.0]hexa-2,5-diene and bis(fluoroxy)difluoromethane yielded four-membered fused-ring-containing perfluoroethers and copolymers. The reaction products were analyzed by gas chromatography, gas chromatography-infrared, gas chromatography-mass spectra, field ionization mass spectra and ^{19}FNMR. The elucidation of the polymer microstructures was assisted by the ^{19}FNMR spectroscopy of the related compounds, hexafluorobicyclo[2.2.0]-hexanes and -hexene in the volatile fraction.

An increase of the concentration of 'Dewar' C_6F_6 in hexafluorobenzene for copolymerization with $CF_2(OF)_2$ decreased the six-membered ring moieties. At about 90% level of the para-bonded C_6F_6, no six-membered ring-containing perfluoroethers were found in the volatile fraction and only a low concentration of the six-membered ring moieties were in the polymeric fractions. The molecular weights of the copolymers ranged from 1000 to over 10,000. The microstructures of the thermal and photopolymers about 1000 range were suggested.

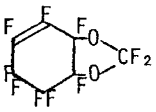
INTRODUCTION

The ease of photoisomerization of perfluoroaromatics to form higher energy valence bond isomers has been widely studied. The para-bonded hexafluorobenzene (I) was reported to form a variety of Diels Alder adducts[1] and undergo many reactions typical of a perfluoroolefin.[2,3]

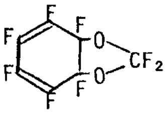


I

In our earlier investigation on the thermal and photopolymerizations of bis(fluoroxy)difluoromethane[4] and hexafluorobenzene, copolymers of molecular weight about 2500 were formed and two new perfluoroethers, 1,2-difluoromethylenedioxyoctafluorocyclohexene-3 (II) and 1,2-difluoromethylenedioxyhexafluorocyclohexa-3,5-diene (III) were identified.[5] The loss of aromaticity of hexafluorobenzene by adduct formation with monofluoroxyperfluoroalkanes was previously reported.[6]



II



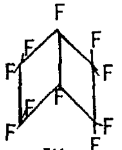
III

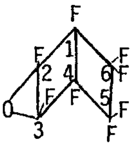
This work continues the study of new perfluoropolymer-forming reactions by copolymerization of hexafluorobicyclo[2.2.0]hexa-2,5-diene (I) and $CF_2(OF)_2$ under thermolysis and photolysis.

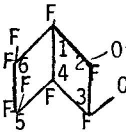
RESULTS AND DISCUSSION

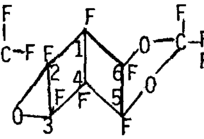
Although $CF_2(OF)_2$ did not readily react with perfluorocycloolefins (e.g., c-C_5F_8 and c-C_6F_{10}),[7] the bisfluoroxyperfluoroalkane formed four-membered fused-ring-containing perfluoroethers and copolymers with 'Dewar' C_6F_6. The increased reactivity of the cyclic olefinic bonds of the strained perfluorodiene molecule (I) is most likely attributed to the strain release as the hybridization changes from sp^2 to sp^3.

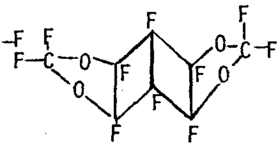
When 95% of I (with 5% hexafluorobenzene) was reacted with an approximately equal mole ratio of $CF_2(OF)_2$ in perfluoropentane solvent at -25°C for 2 hr, the six-membered ring compounds such as II, III, hexafluorobenzene and bis(perfluorocyclohexa-2,5-diene) were not detected in the volatile fraction. After evacuation of the noncondensable gas, traces of very volatile compounds such as CF_4 and COF_2, and the solvent n-C_5F_{12}, the remaining volatile fraction consisted of five perfluorobicyclohexane derivative which were eluted from the gas chromatography column in the following order and ratio: decafluorobicyclo[2.2.0]hexane (IV, 2%), 2,3-epoxyoctafluorobicyclo[2.2.0]hexane (endo-V, 2%), 2,3-difluoromethylenedioxyoctafluorobicyclo[2.2.0]hexane (exo-VI, 12%), 2,3-epoxy-5,6-difluoromethylenedioxyhexafluorobicyclo[2.2.0]hexane (endo, exo-VII, 6%) and 2,3-and 5,6-bis-(difluoromethylenedioxy)hexafluorobicyclo[2.2.0]hexane (exo, exo-VIII, 9%).


IV


endo-V


exo-VI

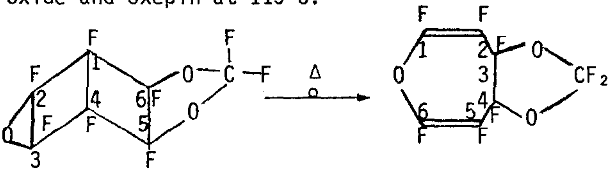

endo, exo-VII


exo, exo-VIII

When the 90% of I (with 10% hexafluorobenzene) was reacted with an excess of $CF_2(OF)_2$ at -40°C under photolysis for 2 hr, the reaction products resembled the above experiment under thermolysis except with a slight decrease of VIII.

The assignments of the difluoromethylenedioxy group for the predominant isomers VI to VIII as an exo-substituent and the epoxy group for the major isomers of V and VII as an endo-substituent were based on their ^{19}FNMR spectra, which are summarized in Tables I to III. The elucidation of structure IV was based on ^{19}FNMR of octafluorobicyclo[2.2.0]hex-2-ene (IX)[8] with the absence of olefinic infrared absorption at 1750 cm^{-1} and the molecular ion at a mass of 262 ($C_6F_{10}^+$) by gas chromatography-mass spectrometry.

The perfluorobicyclohexene oxides V and VII underwent thermal isomerization to form the corresponding cyclic perfluorodivinylene ethers (X and XI in Table III). The thermal ring expansion of the epoxide group of perfluorobicyclohexane (eq. 1) was not without precedent. The rearrangement of 'Dewar' benzene oxide was reported to form an equilibrium mixture of benzene oxide and oxepin at 115°C.[9,10]

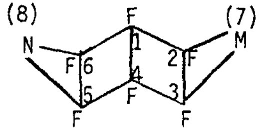

endo, exo-VII XI

(1)

The gas chromatography (2% OV-210 on Chromsorb W column at 100°C with thermal conductivity detector at 200°C) separation of a single peak VII from the volatile fraction showed spectroscopic properties of ^{19}FNMR expected from a mixture of two compounds (endo, exo-VII and XI about 2:3 ratio) suggesting that thermal isomerization was occurring (eq. 1). The sealed NMR tube was then heated to 190°C for 15 min. and the mixture became mainly 3,4-difluoromethylenedioxy-1,6-epoxyhexafluorohexa-1,5-diene (XI) in 95% conversion with the presence of a small amount of white solid. A gas chromatography-infrared analyzer (with the detector

TABLE I

The ^{19}F chemical shift ($\phi CFCl_3$ ppm) of some hexafluorobicyclo[2.2.0]-hexanes and -hexene

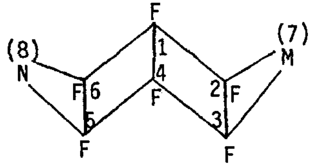


Cpd	Substituent[a] exo-M	exo-N	Spin System	ϕ1,4	ϕ2A,3A endo	ϕ2B,3B exo	ϕ2,3 olefinic	ϕ5A,6A endo	ϕ5A,6B exo	ϕ7A,8A endo	ϕ7B,8B exo
IV	2B 3B -F -F	6B 5B -F -F	$A_4B_4X_2$	201.5	118.4	129.7		118.7	129.7		
VIII	7A 7B $-OCF_2O-$	8A 8B $-OCF_2O-$	A_4X_2	193.2	132.2			132.2		56.5	62.4
VI	7A 7B $-OCF_2O-$	6B 5B -F -F	AA'BB'MM'XX'	197.0	132.1			118.6	128.8	56.5	62.9
XII		8A 8B $-OCF_2O-$	AA'MM'XX'	197.0			123.3	133.7		ϕ8A 51.3	ϕ8B 62.2

[a] "A" designates endo and "B" exo.

TABLE II

The F,F-coupling constant (J Hz)[b] for some hexafluorobicyclo[2.2.0]-hexanes and -hexene



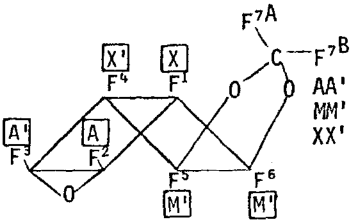
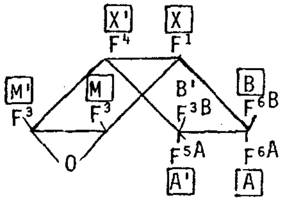
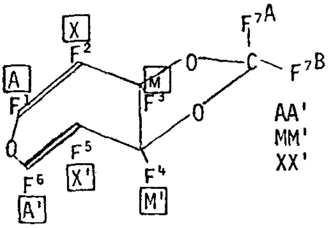
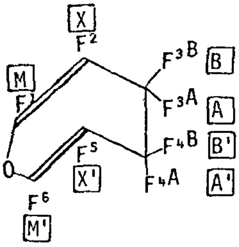
Cpd	Substituent[a] exo-M	exo-N	[1,2A] [3A,4]	[1,3A] [2A,4]	[1,6A] [4,5A]	[1,5A] [4,6A]	[2A,6A] [3A,5A]	[2A,5A] [3A,6A]	[2A,2B] [3A,3B]	[5A,5B] [6A,6B]	[5A,6A] [5B,6B]	[5A,6B] [5B,6A]	[2A,3A]	[1,4]	[7A,7B] [8A,8B]	[7A,2A;7A,3A] [8A,5A;8B,6A]	[7B,2A;7B,3A] [8B,5A;8B,6A]
IV	2B 3B -F -F	6B 5B -F -F	6	6	6	6			235	235							
VII	7A 7B -OCF$_2$O-	8A 8B -OCF$_2$O-	6	6	6	6									60.5	2	5.7
VI	7B 7B -OCF$_2$O-	6B 5B -F -F	6	6	6	6	12	29		241	3	4	12	24	[7A,7B] 60.5	[7A,3A;7A,3A] 2	[7B,2A;7B,3A] 2.5
XII		8A 8B -OCF$_2$O-	[1,2] [3,4] -17.5	[1,3] [2,4] +8.5	-20	+4.5	[2,6B] [3,5B] 0	[2,5B] [3,6B] 0			[5,6] 12		[2,3] 11	2	[8A,8B] 68.6	[8A,5A;8A,6A] 2.5	[8B,5A;8B,6A] 6

[a] "A" designates endo and "B" exo.

[b] J-value signs are relative with an accuracy of ± 1Hz.

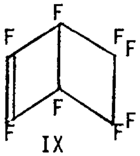
TABLE III

^{19}FNMR of some perfluorobicyclohexene oxides and their valence bond isomers

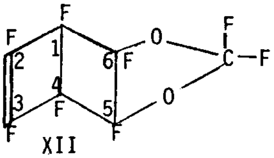
Cpd	Formula	Spin System	Assignment	Chemical Shift (ϕCFCl$_3$ppm)	Coupling Constant J(Hz)
VII			F(7A)endo	56.0	J(7A,7B)=67.3; J(7B,6)=J(7B,5)=5.5; J(1,2)=J(3,4)=12; J(3,5)=J(2,6)=8; J(1,6)=J(4,5)=12
			F(7B)exo	63.9	
		AA'	F(2,3)exo	181.5	
		MM'	F(5,6)endo	129.6	
		XX'	F(1,4)		
V		MM'	F(2,3)exo	181.6	
		AA'	F(5A,6A)endo	119	
		BB'	F(5B,6B)exo		
		XX'	F(1,4)	199.5	
XI			F(7A)endo	56.1	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
			F(7B)exo	61.8	
		AA'	F(1,6)	93.3	
		MM'	F(3,4)endo	111.2	
		XX'	F(2,5)	176.9	
X		MM'	F(1,6)	96.3	
		AA'	F(3A,4A)endo	119	
		BB'	F(3B,4B)exo		
		XX'	F(2,5)	181.3	

and IR cell maintained at a temperature of 180°C, an injection port at 160°C and a stainless steel column with OV-210 on Chromsorb W at 100°C) was used to record the infrared absorption of VII and XI. The decreasing absorbance at 1540 cm^{-1} (i.e. the epoxide group of VII) was observed with respect to time and with a new absorbance increasing at 1755 cm^{-1} (i.e. the olefinic bonds of XI). A plot of the log values of the absorbance at 1540 cm^{-1} versus time showed the first order dependence as the absorbance at 1755 cm^{-1} versus time over the same period of about 20 min for the conversion of VII to XI. The half life of VII at 180°C was 6 min. The gas chromatography-mass spectrometry of the unisomerized molecule (VII) had a molecular ion at a mass of 284 ($C_7F_8O_3^+$).

Under photolytic condition at -40°C with the concentration of I in hexafluorobenzene decreasing to 70% at approximately equal mole ratio of I to $CF_2(OF)_2$, the absence of noncondensable gas was noted. This was due to the increasing amount of hexafluorobenzene, which apparently functioned as a fluorine atom acceptor as well as the third monomer. The reaction products were different from the above experiments. The six-membered ring-containing compounds and a new isomer XII (exo-5,6-difluoromethylenedioxyhexafluorobicyclo[2.2.0]hex-2-ene) were found, while the perfluorobicyclohexane (IV) and the epoxy-derivatives (V and VII) were absent.



IX



XII

The order and ratio of the elutes from the gas chromatography column were as follows:

VI (5%), II (10%), III (20%), XII (7.5%), VIII (3.6%),
II (0.9%), hexafluorobenzene (9.8%), and bis(perfluorocyclohexa-2,5-diene) (0.9%).

In all cases I was notably absent among the products. The residual colorless liquid (vapor pressure less than 1 mm Hg at 25°C) was polymeric (45 to 75% yield). A decrease of six-membered ring moieties was observed with increasing concentration of I (70 to 95% with the presence of hexafluorobenzene). The moelcular weights of the polymer fractions were determined by gas chromatography at 250°C with 3 to 4 atm of helium as carrier gas. The molecular weights of the known fluorocarbon ether ploymers were used as the standards (Figure 1).

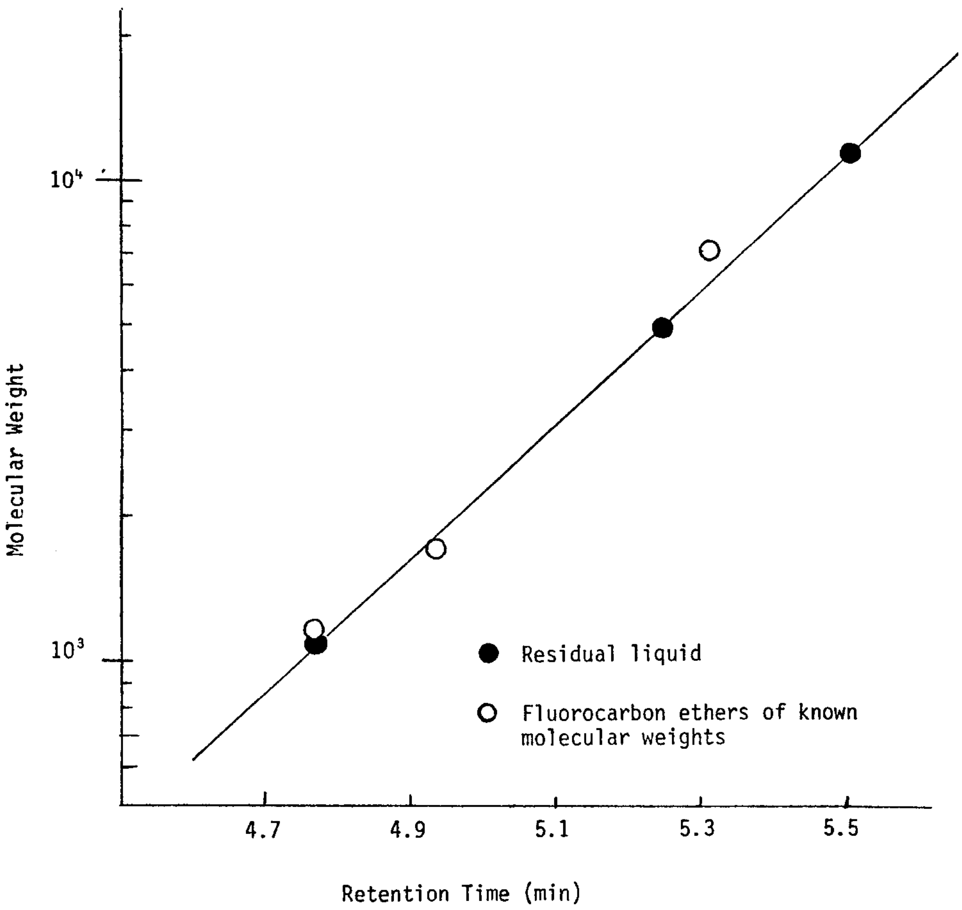
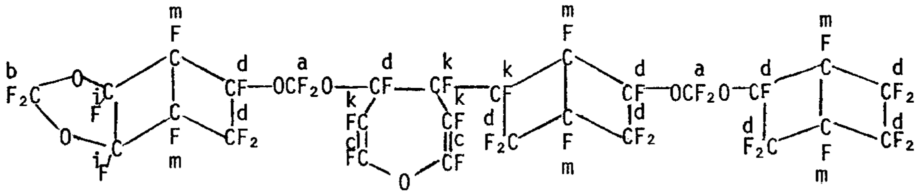


Figure 1 Retention time and molecular weight relationships of fluorocarbon ethers.

Table IV summarized the ^{19}FNMR data of the copolymers at 1000 molecular weight range. The tentative structures deduced from Table IV were suggested below:

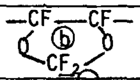
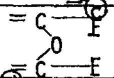
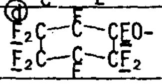
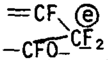
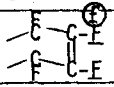
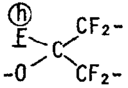
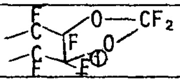
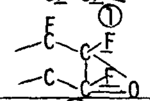
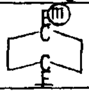


XIII

Thermal polymer (moelcular weight ~ 1100)

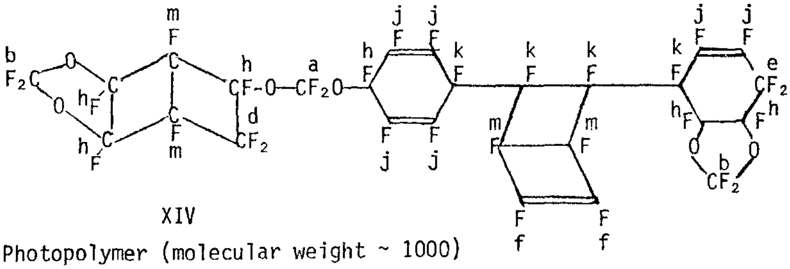
TABLE IV

^{19}FNMR data of copolymers

Polymer Group & Assignment	Chemical Shift $\phi CFCl_3$(ppm)	Number of Fluorines in Polymer Groups: Thermal Polymer Measured*	Thermal Polymer Theoretical**	Photopolymer Measured*	Photopolymer Theoretical**
ⓐ $-OCF_2O-$	49-54	3	4	3	2
 ⓑ	59-64	3	2	3	4
 ⓒ	74-95	2	2		
 ⓓ	118-129	15	16	2	2
 ⓔ	120			2	2
 ⓕ	124			2	2
ⓖ $-CF_2-$	120-130			6	6
 ⓗ	127-145				
 ⓘ	130-135	2	2		
ⓙ $-CF=CF-$	147-160			6	6
ⓚ $=CF-CF=$	160-175	2	4	3	4
 ⓛ	162-181				
 ⓜ	194-197	4	6	4	4

* Relative area

**Based on suggested structures for thermal and photopolymers, XIII and XIV respectively.



XIV

Photopolymer (molecular weight ~ 1000)

The infrared spectra of the polymer product suggested the presence of the olefinic bonds decreasing with the increasing concentration of 'Dewar' C_6F_6 and increasing with the increasing concentration of hexafluorobenzene.

^{19}FNMR spectra

The results of the ^{19}FNMR spectral data of hexafluorobicyclo[2.2.0]-hexanes and -hexene are summarized in Tables I and II and the perfluorobicyclohexene oxides and their thermally isomerized isomers in Table III. The assignments were assisted by the previously reported hexafluorobicyclo-[2.2.0]-hexanes and -hexenes.[8,11] The assignment of the endo-fluorines downfield from the exo-fluorines is in agreement with Barlow et. al.[8] and also consistent with the idea of the endo being pseudo axial and the exo being pseudo equatorial. It can be seen in Tables I and II that all the compounds contain the tertiary endo-fluorines, which absorb in the range 128 to 134 ppm and the bridgehead fluorines, which absorb in the range of 193 to 202 ppm.[8] The literature values of the bridgehead fluorines of IX and I were 199.9 and 191.0 ppm respectively.[12,13]

The difluoromethylenedioxy groups are an AB-type and absorb in the range of 51 to 57 ppm for the endo-fluorines and in the range of 62 to 63 ppm for the exo-fluorines. Our previously reported values of the difluoromethylenedioxy groups for II and III were also an AB-type and absorb in the range of 51 to 58 and 61 to 63 ppm.[5] For the 1:1 adduct (exo-VI) the AB-type absorption was observed at 118.6 ppm for the endo-fluorines (F^{5A} and F^{6A}) and at 128.8 ppm for the exo-fluorines (F^{5B} and F^{6B}).

We took as a basis for our structural assignments for the 2,3-and 5,6-bis(difluoromethylenedioxy)hexafluorobicyclo[2.2.0]hexane as the exo-2,3-and exo-5,6-isomer(VIII). The alternatives of an exo-2,3-and endo-5,6-isomer was ruled out for the symmetry reasons and of an endo-2,3-and endo-5,6-isomer was ruled out by steric crowding as well as the lack of spatial couplings between F^7 and F^8. The assignment of the exo-2,3- and exo-5,6-isomer (VIII)

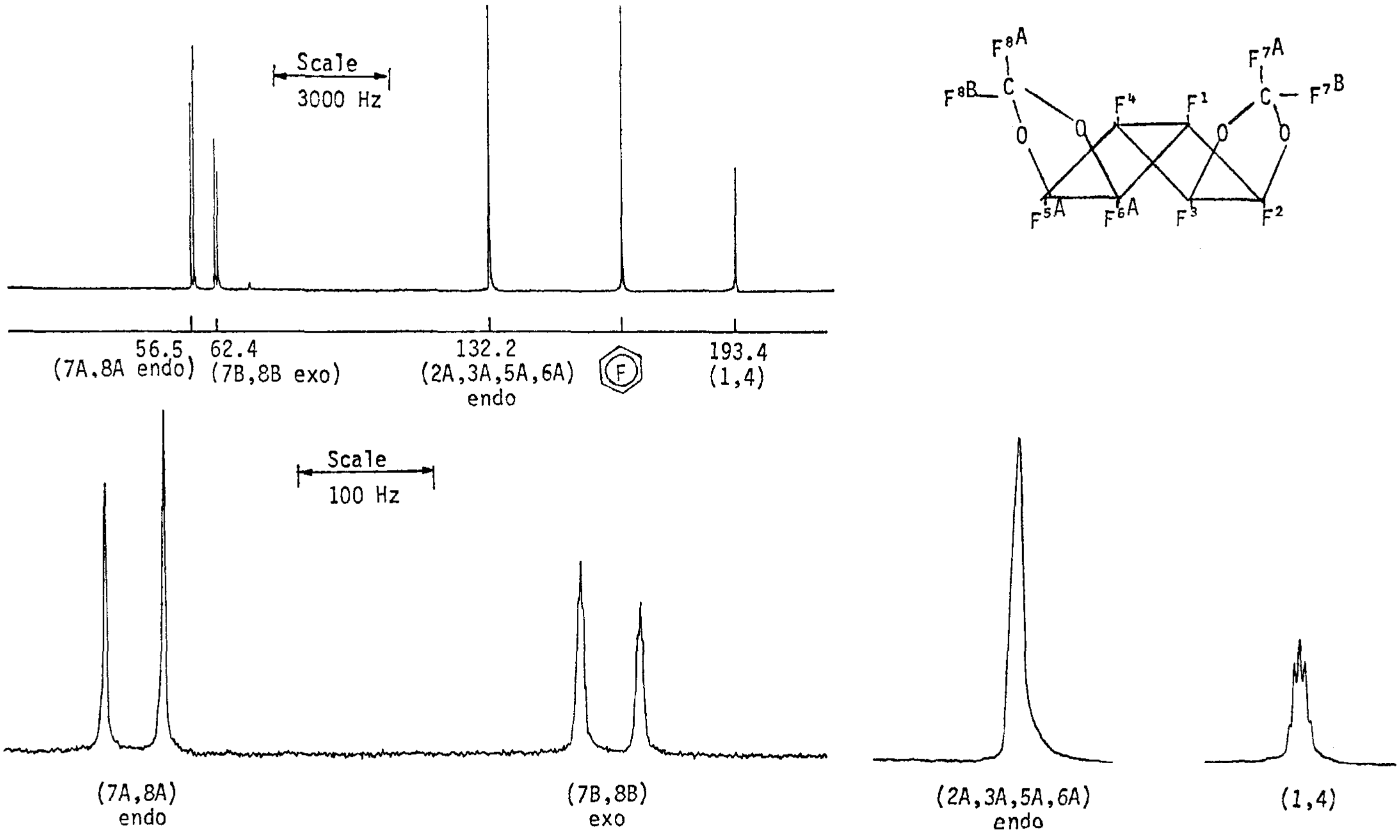


Figure 2. The ^{19}FNMR spectrum of exo-2,3-and exo-5,6-bis(difluoromethylenedioxy)hexafluorobicyclo[2.2.0]hexane

was provided by the simple A_4X_2 nature of the spectrum (Figure 2). Its bridgehead fluorine ($F^{1,4}$) at 193.4 ppm showed a quintet with the equivalent J-values at (1,2A; 3A,4) (1,3A; 2A,4) (1,6A; 4,5A) (1,5A; 4,6A) of 6Hz (VIII in Table II). The assignment of these J-values were confirmed by the ^{19}F-decoupling techniques and by computer analysis using the two resonances. One irradiation at 62.4 ppm (F^{7B} and F^{8B} of VIII in Table I) of the singlet at 132.2 ppm (the tertiary endo-fluorines at F^{2A}, F^{3A}, F^{5A} and F^{6A}) yielded a triplet (J-6Hz). The other irradiation at 132.2 ppm of the quintet at 193.4 ppm ($F^{1,4}$) yielded a triplet (J-6Hz). Thus the ^{19}F decoupling confirmed the symmetry of VIII and its exo-, exo- nature of the substituents of VIII. All the 6Hz J-values (Table II) have the same sign; while the other J-values could be any reasonable value and may have "+" or "-" signs without purturbing the spectrum, when the computer six spin system is used. This is because of the magnetic equivalence of F^2, F^3, F^5 and F^6 and the magnetic equivalence of F^1 and F^4.

The ^{19}FNMR spectra of VI and XII (Figures 3 and 4) were more complex than VIII. Likewise the ^{19}F-decoupling techniques were necessary to aid the structural elucidations. The assignments of the J-values[15] were assisted. by the computer programs (Tables I and II). The partially elucidated ^{19}FNMR of perfluorobicyclohexene oxides (VII and V) and their thermal isomers (X and XI) are summarized in Table III.

Mass spectra

The gas chromatography-mass spectral data showed distinctive molecular ions of XII and the endo-2,3-and exo-5,6-isomer of VIII with strong m/e values at 268 and 350 respectively; while the predominant isomer VIII (i.e., exo-2,3-and exo-5,6-isomer) only showed a very weak molecular ion at m/e value 350 and VI (i.e., exo-2,3-isomer) gave the highest m/e value at 287 (i.e., mass of parent ion 306 minus 19 for fluorine). The attempted mass spectroscopic (CEC21-110-B) molecular weight determinations and the field ionization mass spectra of the latter two exo-isomers were unsuccessful. The general mass cracking patterns of VI resembled VIII and of the two VIII isomers were almost alike except with the lack of the molecular ion for the major exo-2,3-and exo-5,6-isomer.

Mass spectroscopic molecular weight (CEC21-110-B) of exo-XII: Found, 267.9770. Calculated for $C_7F_8O_2$: 267.9975.

Mass spectroscopic molecular weight (CEC21-110-B) of exo, endo-VIII: Found, 349.9623. Calculated for $C_8F_{10}O_4$: 349.9637.

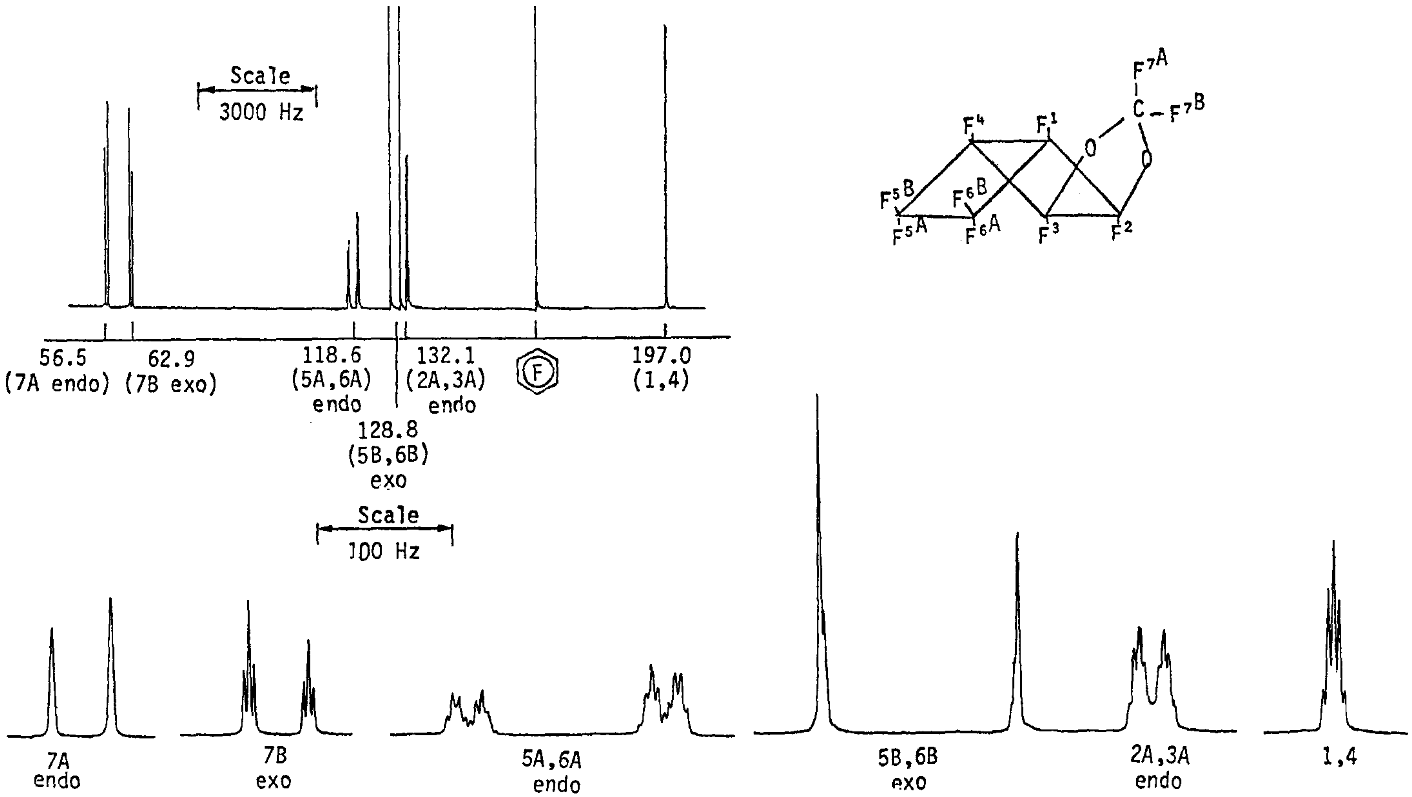


Figure 3 The ^{19}FNMR spectrum of exo-2,3-difluoromethylenedioxyoctafluorobicyclo[2.2.0]hexane

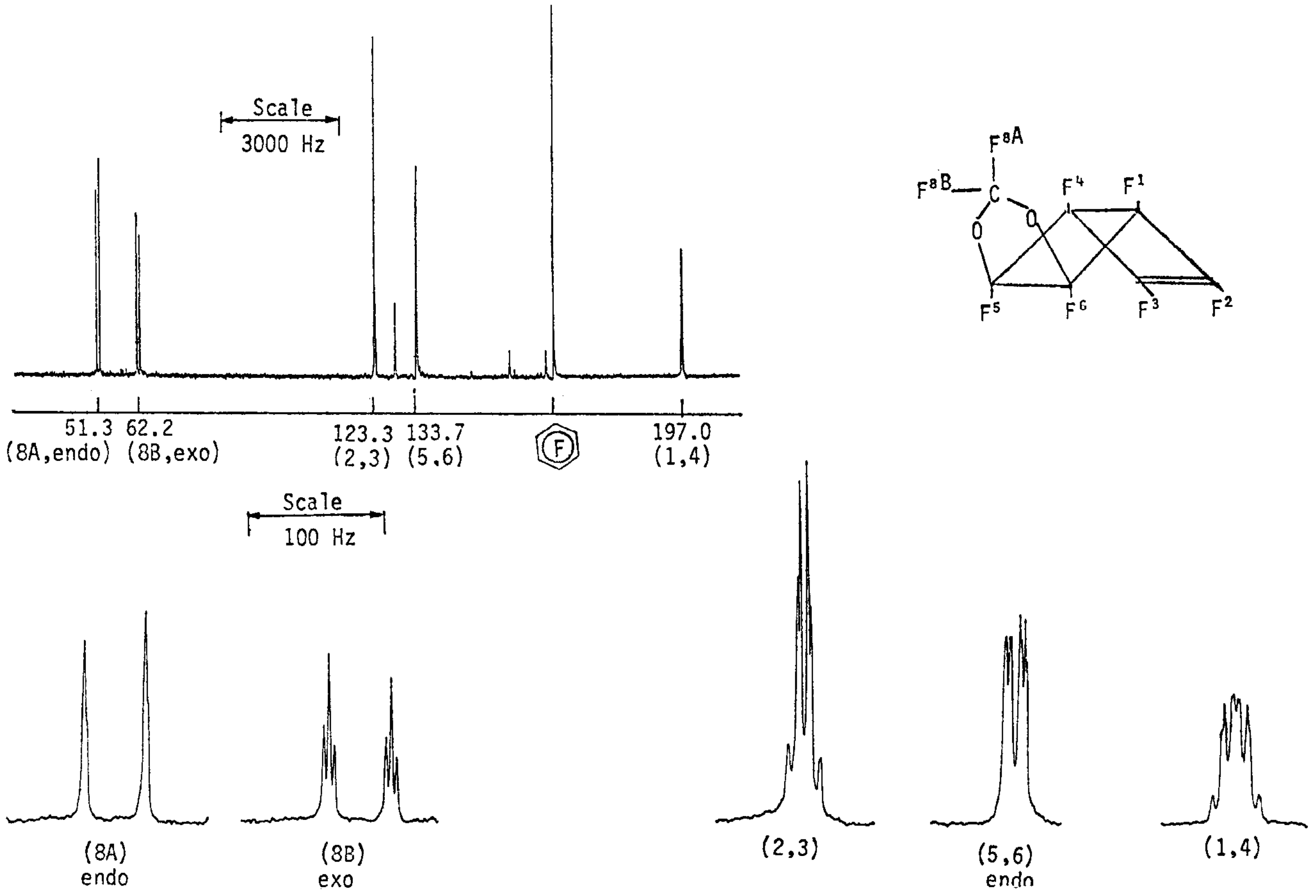


Figure 4. The ^{19}FNMR spectrum of exo-5,6-difluoromethylenedioxyhexafluorobicyclo[2.2.0]hex-2-ene

EXPERIMENTAL

Material and apparatus

Hexafluorobenzene and perfluoropentane were purchased from PCR. The 'Dewar' C_6F_6 and $CF_2(OF)_2$ were prepared as previously described.[2,4] The reactants and solvents were checked by infrared and ^{19}FNMR spectroscopy. I was also checked by gas chromatography.

The infrared spectra were measured on a Perkin Elmer 567 spectrophotometer and with a chromatographic infrared analyzer (CIRA 101). The ^{19}FNMR spectra were recorded by a Varian XL-100 spectrometer operating at 94.1 MHz and 35°C using hexafluorobenzene as an external reference. The ^{19}F chemical shifts were then converted to $CFCl_3$ as the reference using the value of 164.9 ppm for hexafluorobenzene. A Gow Mac gas chromatography (Model 69-550) with an enlarged oven was used to accommodate the 6m x 2mm spiral glass column which was packed with 2% OV-210 on Chromsorb W and were run at 50 to 250°C with 3 to 4 atm helium as carrier gas. Mass spectra were obtained from an LKB9000 mass spectrometer, which has an ionizing potential of 70eV and a resolving power of 2000. The mass spectra for the molecular ions were run by LKB9000 mass spectrometer at 13eV and the field ionization mass spectrometer. The gas chromatography-mass spectra were also run on the LKB9000 instrument, using the same column as described under gas chromatography. The elemental analyses were determined by the CEC21-110-B mass spectrometer.

Procedure

In a typical run, $CF_2(OF)_2$ (7 to 20 mmol) was slowly added by increments for a period of 1 to 3 hr and vacuum manipulation to a solution of varied mole ratio of 'Dewar' C_6F_6 (from 70% to 95% I in hexafluorobenzene) in an excess perfluorocarbon solvent such as n-C_5F_{12}. For the thermal reactions, $CF_2(OF)_2$ was added slowly to a solution maintained at -25°C and consisted of 'Dewar' C_6F_6 solution in an excess of n-C_5F_{12}. The liquid then stood overnight between 0° to 10°C, warmed and stirred at 25°C, before it was chilled and evacuated at -196°C. The last two steps in warming and stirring at 25°C and evacuating at -196°C were sequentially repeated, until the absence of noncondensable gas persisted at -196°C. A quartz reaction vessel was used for the photolytic reactions and was maintained at -40°C by an alcohol coolant bath in a quartz Dewar flask that allowed the passage of ultraviolet light. A 200-watt high pressure mercury arc lamp was utilized as an outside irradiation source for a period of 2 hr.

The product mixtures were evacuated at -196°C for the noncondensable gas and progressively warming from -196° to -25°C for removing the traces of the decomposition products and mainly n-C_5F_{12} solvent. The distillate was periodically monitored by infrared analyses. The distillate collected in the liquid nitrogen trap between -25° to 25°C, till the vapor pressure reached less than 1 mm Hg at 25°C,was the volatile fraction. The volatile fraction (25 to 55% yield) was subsequently fractionated and identified by gas chromatography, gas chromatography-infrared analyzer, gas chromatography-mass spectrometry and ^{19}FNMR. The elemental analyses were determined by mass spectroscopic CEC21-110-B and the molecular weights by the field ionization mass spectra or LKB9000 instrument at 13eV. The microstructures of the polymeric fractions were characterized by ir and ^{19}FNMR spectra and the molecular weights of the polymers by gas chromatography up to 250°C

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