Journal of Fluorine Chemistry, 63 (1993) 59–68

Aromatization of 2 + 2 cycloadducts of butadienes and fluoroolefins other than tetrafluoroethylene*

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(Received April 28, 1992; accepted November 10, 1992)

Abstract

The 2 + 2 cycloadducts of fluorinated olefins other than tetrafluoroethylene and hydrocarbon dienes also ring-expand and eliminate two moles of hydrogen halide to form aromatic products. The hydrogen halide eliminated from chlorofluoroolefin adducts depends on the solid present during the aromatization. Alumina and other accelerators favor elimination of HF, while HCl evolves in the presence of inert solids such as SiC. The aromatics derived from hexafluoropropene adducts generally have the more sterically hindered regiochemistry. Alumina promotes extrusion of difluorocarbene from trifluoromethylcyclobutanes leading to fluorobenzenes rather than benzotrifluorides. Carbon accelerates these aromatizations without difluorocarbene extrusion.

Introduction

In our previous paper [1], we showed that the mechanism for the ring-expansion aromatization of 2 + 2 cycloadducts of tetrafluoroethylene and hydrocarbon dienes was not straightforward. Pyrolysis of the cyclobutanes can begin by rupturing different cyclobutane bonds depending on the substituents and pyrolysis environment.

In this paper, we discuss the aromatization of the 2 + 2 cycloadducts of hydrocarbon dienes and 1,1-difluoroolefins other than tetrafluoroethylene. This additional variable allows even more flexibility in designing syntheses of substituted fluorobenzenes.

Results

Butadiene and other fluoroolefins

$F_2C=CFCl$

We prepared the two stereoisomeric 2 + 2 cycloadducts (**1**) by heating chlorotrifluoroethene (CTFE) and butadiene in a sealed tube with a polymerization inhibitor [2].

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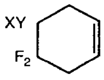
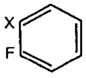
0022-1139/93/$6.00

Pyrolysis of **1** over SiC gave a cyclohexene, **2**, at 450 °C in excellent yield at about 30% conversion. We did not determine the location of the double bond. At 600 °C, loss of two moles of HX gave *ortho*-substituted fluorobenzenes. The product composition was 72% 1,2-difluorobenzene (**3**); 16% 1,2-fluorochlorobenzene (**4**); and 7% fluorobenzene (**5**). We also found 5% of 1,3-fluorochlorobenzene (**6**). The solid present during the pyrolysis can influence the product distribution. In the presence of alumina at 350 °C, **1** completely reacted giving 35% **3**; 35% **4**; 5% **5**; and 26% **6**. There were also traces of aromatic products with CF_3 groups.

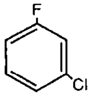
1 X=F Y=Cl
7 X=F Y=Br
8 X=Cl Y=Cl
11 X=F Y=H



2 X=Cl Y=F
10 X=Cl Y=H
12 X=F Y=H



3 X=F
4 X=Cl
5 X=H



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Both zinc oxide and bismuth oxide on alumina also promote aromatization at 400 °C and gave 70% chlorofluorobenzenes and only 30% difluorobenzenes. These solids produced *two* isomers of both difluorobenzene and fluorochlorobenzene which by ^{19}F NMR spectroscopy were *ortho* and *meta*. Neither reagent produced either 1,4-difluorobenzene or 1,4-fluorochlorobenzene.

$F_2C=CFBr$

Passing $F_2C=CFBr$ and butadiene down a hot tube filled with SiC at 400 °C gave two 2+2 cycloadducts, **7**. Aromatization occurred at 600 °C. The major product (~70%) was **3** from the elimination of HF and HBr. The second largest product was C_6H_5F (**5**) and there were only traces of C_6H_4FBr.

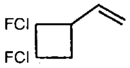
Pyrolysis of the preformed 2+2 cycloadducts **7** with SiC also gave no bromine-containing aromatics. However, pyrolysis over Al_2O_3 at 300 °C produced a mixture of 47% 1,2-, 28% 1,3-C_6H_4FBr and 25% **3**.

$F_2C=CCl_2$

Passing $F_2C=CCl_2$ and C_4H_6 over SiC at 600 °C gave 85% **4**, 11% **5** and 4% **3**. We prepared the 2+2 cycloadduct **8** from $F_2C=CCl_2$ and C_4H_6 by Bartlett's procedure [3a]. The major product from the pyrolysis of **8** over silica–alumina at 350 °C was also **4**. Minor products included **5** and 1,3-C_6H_4FCl (**6**).

$FClC=CFCl$

Passing $FClC=CFCl$ and butadiene over SiC gave all four possible 2+2 adducts, **9**, at 400 °C. These result from the *cis* and *trans* olefin and the two possible orientations of the vinyl group relative to a ring fluorine. The aromatic products at 600 °C are 83% **3**, and about 8% each of **4** and **6**.



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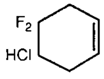

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$F_2C=CHCl$

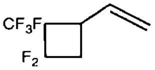
Passing butadiene and $F_2C=CHCl$ over SiC at 600 °C produces 77% **5** and 12% **4**. The 2+4 adduct, **10**, is still present at the 5% level.

$F_2C=CFH$

Passing $F_2C=CFH$ and butadiene over SiC gave four 2+2 adducts, **11**, at 400 °C, a single 2+4 adduct, **12**, at 500 °C, and 92% **5** and 8% **3** at 600 °C.

$F_2C=CFCF_3$

Passing $F_2C=CFCF_3$ (HFP) and butadiene over SiC gave two major 2+2 cycloadducts, **13**, and two minor regioisomers at 400 °C. At 500 °C, the major product was the 2+4 cycloadduct, **14**. At 600 °C, about 50% of the product was still **14**, but two aromatics, **15** and **3**, comprised the balance in the ratio of 3.5:1. The ^{19}F NMR data for **15**, an A_3X with shifts at −62 and −115 ppm, are consistent with 2-fluorobenzotrifluoride [4].



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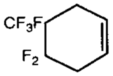

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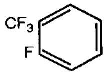

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The preformed 2+2 adducts, **13**, ring-expand thermally at 600 °C to give **14** and **15** as the major products, with a minor amount of **3**.

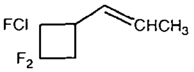
In the presence of Al_2O_3 the rate of disappearance of **13** greatly increases. At 300 °C, there was a significant cycloreversion to $CF_3CF=CH–CH=CH_2$ and $F_2C=CH_2$, identified by GC/MS analysis. At 400 °C, the liquid products are completely aromatic, but heavily cracked: 45% **3**; 46% **5**; and only 21% **15**. Passing **13** over carbon at 500 °C produces mostly **3**.

CTFE and other dienes

1-Methylbutadiene

1-Methylbutadiene and CTFE react in the liquid phase to form four isomers of **16**. By analogy with the TFE results, we expect that the methyl group is on the remaining double bond [1]. Passing **16** over SiC at 550 °C gives two 2+4 adducts, **17**, and aromatics. Because of the large upfield shift of the CFCl relative to the CTFE/butadiene adduct, **2**, we assign **17** as the two isomers with adjacent CH_3 and CFCl groups. The isomers 2,3-difluorotoluene, **18**, and 3,4-difluorotoluene, **19**, are present in the ratio 63:13 along with 24% of **3**. All three isomers of fluorotoluene are present along with several isomers of fluorochlorotoluene. ^{19}F NMR spectroscopy does not detect chlorotoluenes. In the presence of Al_2O_3, no starting material is left at

400 °C. The products are a complicated mixture of difluorotoluenes, fluorotoluenes and fluorochlorotoluenes. The **18/19** ratio is 9:1.



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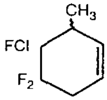

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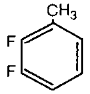

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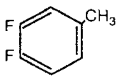

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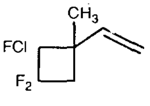
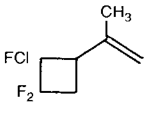
2-Methylbutadiene

2-Methylbutadiene and CTFE give four 2+2 cycloadducts, **20**, in the ratio of 45:32:11:11. Passing **20** over SiC at 500 °C gives both cyclohexenes and aromatic products. Both cyclohexenes seem to be 2+4 Diels–Alder adducts of CTFE and 2-methylbutadiene, **21** and **22**, because of the similarity of these chemical shifts to the butadiene/CTFE adduct **2**. The difluorotoluenes **18** and **19** are present in the ratio of 1:4. Neither **21** nor **22** can be the precursor of 2,3-difluorotoluene (**18**). This product must result from an alternative ring-expansion mechanism.

At 400 °C, in the presence of alumina, the product is entirely aromatic. We have not sorted through the assignments of all the possible isomers of the fluorochlorotoluenes. The total integral of fluorochlorotoluenes versus difluorotoluenes is 7:1.



20a



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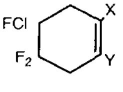
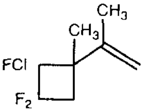


21 X = CH_3 Y = H
22 X = H Y = CH_3

2,3-Dimethylbutadiene

The 2+2 cycloadduct of CTFE and 2,3-dimethylbutadiene, **23**, ring-expands to give 90% of one cyclohexene isomer at 525 °C. We assign the structure as the Diels–Alder product **24** by the same reasoning used for the 2-methylbutadiene adducts, **21** and **22**. At 600 °C, the product contains two difluoroxylenes with NMR singlets at −144 ppm (major) and −143 ppm (minor). The major one is 4,5-dimethyl-1,2-difluorobenzene, the minor one is 1,2-difluoro-3,6-dimethylbenzene [1]. The reaction produces the same difluoroxylenes in the presence of alumina at 350 °C. However, alumina directs the product more toward chlorofluoroxylenes rather than difluoroxylenes. The proton-decoupled, ^{19}F NMR data for chlorofluorotoluenes are all singlets and cannot be assigned to specific isomers without more work.



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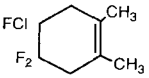
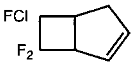


24

Cyclopentadiene

The 2 + 2 cycloaddition gives two isomers each of bicycloheptene, **25**, and norbornene, **26**. There is little preference for either the *exo* or *endo* isomer involving the CFCl group. Pyrolysis of this mixture over SiC does not give any cycloheptadienes. Under conditions where **25** is consumed and **26** survives, the major product is fluorobenzene **5**.



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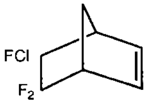
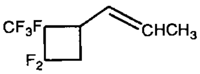


26

HFP and other dienes

1-Methylbutadiene

HFP reacts with 1-methylbutadiene to give mixtures of the 2 + 2 adducts, **27**. The cycloadducts both ring-expand thermally at 500 °C and in the presence of carbon at 450 °C to give one major aromatic product. The proton-decoupled ^{19}F NMR spectrum is of an A_3X type with chemical shifts at -56.1 and -113.7 ppm, $J_{FF} = 27$ Hz. The trifluoromethyl resonance is 7 ppm downfield from that of **15**, and the F–F coupling increases from 13 to 27 Hz. Steric compression can lead to increased coupling and the downfield shift [5]. We assign the structure as the more sterically crowded aromatic 3-fluoro-2-trifluoromethyltoluene, **28**. There are minor amounts of several products resulting from difluorocarbene extrusion. Pyrolysis in the presence of SiC at 500 °C also gives small amounts of all four isomers of $CF_3CF{=}CH{-}CH{=}CHCH_3$ and two cyclohexene isomers.



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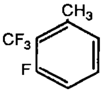
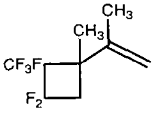


28

2,3-Dimethylbutadiene

HFP reacts with 2,3-dimethylbutadiene in the liquid phase at 180 °C to form two 2 + 2 cycloadducts, **29**, and a Diels–Alder product, **30**. Passing **29** over SiC at 550 °C gave complete conversion to three products. The major product was cyclohexene, **30**. The NMR spectrum of one of the minor products was of an A_3X type with chemical shifts at -61.4 and -120.7 ppm, $J_{AX} = 13$ Hz. The ring fluorine chemical shift and the coupling constant suggests no adjacent methyl groups. The most likely structure is 2-fluoro-4,5-dimethylbenzotrifluoride (**31**).

The other minor product was characterized as a *ring-opened material*, $CF_3CHFCF_2CH_2CHMeCMe{=}CH_2$ (**32**) by a combination of ^{19}F NMR and GC/MS methods. The molecular weight (by GC/MS) was consistent with the addition of H_2, rather than a dehydrogenation product. ^{19}F NMR spectroscopy showed three resonances at −74.4 (d, $J_{FF}=10$ Hz, CF_3) and −209.4 ppm (q, $J_{FF}=10$ Hz, d, $J_{HF}=$ 44 Hz, CFH) and an AB pattern at −106.9 and −109.7 ppm, $J_{FF}=210$ Hz, CF_2. Carbon, but not solid oxides, accelerates the aromatization of **29**. The major product is again **31**.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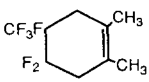
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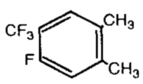
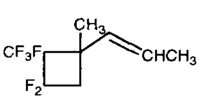

31

1,3-Dimethylbutadiene

The liquid-phase reaction of HFP and 1,3-dimethylbutadiene gives six products. Four are 2 + 2 adducts, **33**, and two are 2 + 4 adducts, **34**. Pyrolysis of this mixture at 600 °C over SiC consumes all of **33**, and produces two aromatic products. From the NMR spectra, the major aromatic is 2,4-dimethyl-6-fluorobenzotrifluoride (**35**). The NMR spectrum had a CF_3 resonance at −55.9 ppm and aromatic CF at −114.8 ppm with $J_{AX}=27$ Hz, characteristic of steric compression. Also prominent are difluorotoluenes **18** and **19** and difluoroxylenes from the extrusion of difluorocarbene. None of the typical solids accelerated this reaction.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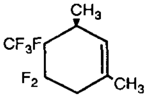
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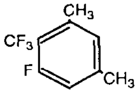
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2-Chlorobutadiene

2-Chlorobutadiene and HFP form four 2+2 cycloadducts, **36**, at 175 °C. Cyclobutanes **36** do not form aromatics with CF_3 groups at 400 °C in the presence of SiC. In the presence of carbon at 400 °C, the pyrolysis produces several isomers of $CF_3C_6H_3FCl$. These aromatics form with SiC only above 550 °C. Loss of difluorocarbene to give chlorodifluorobenzenes is a significant side-reaction. We have not assigned specific structures to the isomers of the fluorochlorobenzotrifluorides produced.

Discussion

Chemoselectivity

Cycloadducts of TFE and hydrocarbon dienes aromatize by the loss of two moles of HF [1]. Cycloadducts from CTFE and dienes ring-expand and aromatize by losing two moles of HX. One mole of HF must be eliminated from the CF_2 group. The halide lost from the CFCl group depends on the solid present during the pyrolysis. HCl is the thermal elimination product from chlorotrifluoroethene 2+2 cycloadducts. HF elimination preferentially occurs in the presence of solid-acids. Carbon catalyzes the ring-expansion elimination to give mostly **15** at 500 °C, while most acidic materials either show no rate enhancement or promote loss of difluorocarbene.

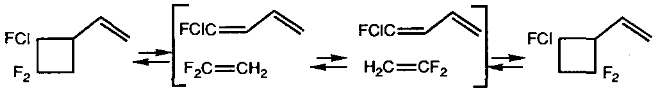
Regiochemistry

The specific aromatic isomer formed during the ring-expansion elimination depends both on the substitution pattern of the cyclobutane and the solid present during the pyrolysis. The aromatization products from HFP adducts result in the more sterically hindered products. Alumina enhances the formation of the difluorotoluene expected from the Diels–Alder ring-expansion.

Origin of 1,3-dihalobenzenes

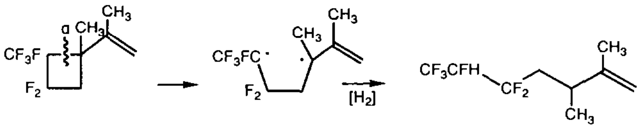
Difluorobenzene isomerizations only occur at temperatures well above those used in this work [6]. No catalyst for this reaction has ever been reported. It is unlikely that the 1,3-difluorobenzene comes from an initially formed *ortho* isomer. Fluorochlorobenzene isomerization occurs in the presence of Brønsted acids by 1,2-shifts [7]. The observation of only small amounts of *meta* and no *para* fluorochlorobenzene could be the result of a slow 1,2-shift mechanism.

Another possibility is that some intermediate isomerizes to the penultimate precursor of the *meta* isomers. One possibility begins with a 2 + 2 cycloreversion of **1** to $H_2C{=}CF_2$ and $H_2C{=}CH{-}CH{=}CFCl$. Readdition of these two materials *in the opposite direction* followed by ring-expansion and aromatization provides a specific path to metadihalobenzenes.



The ring-opened product from HFP and 2,3-dimethylbutadiene

A hydrogen addition to the intermediate diradical from breaking bond a could lead to this product.



Tropolone problem

In contrast to the cycloadducts of TFE and cyclopentadiene, those from CTFE and cyclopentadiene do not give any seven-membered rings on pyrolysis. Beginning with the same mechanism which explained the TFE products [1], we postulate that the initial bond which breaks is the one which produces $\cdot CFClCF_2$. This radical rapidly loses :CFCl and the six-carbon diradical aromatizes.

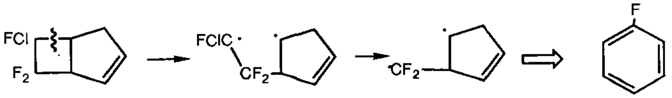


TABLE 1

^{19}F NMR parameters for 2+2 cycloadducts[a]

Compound	δ_1 (ppm)	δ_2 (ppm)	J_1 (Hz)
1	100.0 117	111	194
	135 108.0	106.0	195
7	133.9 100.5	93.5	195
	109.0 118.6	108.7	195
8	105.5 97.6	–	184
9	94.9 119.9 108.1 120.1	99.3 106.7 111.0[b] 133.3[b]	
11	106.6 115.9	194.4 –	204
	94.7 115.2	192.9 –	207
	189.7 –	92.5 125.6	202[b]
	202.7 –	92.5 137.6	200[b]
13	191 79.5	107 109	220[b]
	171 75.6	101 118.5	220[b]
	100 103	177 79.0	220
	123.4 128.2	183 80.3	210
16	118.8 99.9	111.4	195
	118.9 99.3	109.9	195
	109.4 135.9	107.3	198
	109.1 135.4	106.9	198
20	131.4	105.1 107.7	202
	121.5	113.1 96.6	196
	124.2	122.5 94.9	195
20	137.5 98.4	118.3	195
	123.0 98.2	108.9	199
	126.0 101.2	107.4	201
23	105.1 107.7	131.4	202
	96.6 113.1	121.5	196
25	124.2 94.9	122.5	195
	118.4 113.0	106.4	199
27	109.2 106.1	190.2 79.8	215
	108.8 106.8	190.8 79.8	215
	100.7 118.0	170.5 76.2	211
	101.3 118.0	171.5 75.7	211
29	74.6 180.1	98.9 111.8	216
	73.5 184.1	106.9 109.3	215
33	74.9 182.7	110.4 111.8	216
	76.3 170.4	100.9 118.1	213
	79.6 190.4	106.5 109.1	215
36	75.1 175.6	101.9 109.5	220
	74.9 168.8	107.6 109.3	216
	74.2 168.3	102.2 110.3	217
	78.7 192.1	101.6 118.4	213

[a] All shifts are upfield of the reference $CFCl_3$.

[b] Partners may be reversed.

TABLE 2

^{19}F NMR parameters for 2+4 cycloadducts[a]

Compound	δ_X (ppm)	δ_Y (ppm)	J_{AB} (Hz)	Compound	δ_X (ppm)	δ_Y (ppm)	J_{AB} (Hz)
2	112.0 114.0	124.2	240	**22**	114.8 *	123.4	246
10	101.3 107.3		240	**24**	111.9 114.9	123.6	246
12	109.4 110.9	198.0	251	**26**	111.1 97.6	110.5	217
	109.8 114.2	205.7	245		112.6 100.3	113.5	215
14	110.5 114.0	77.3 180.8	260	**30**	77.2 180.0	110.8 114.8	254
17	108.9 112.3	135.3	250	**34**	72.5 172.0	107.8 109.4	266
	111.4 116.6	133.3	241		73.2 194.0	110.8 110.8	–
21	111.7 113.7	124.9	246				

*Not observed.

[a] All shifts are upfield of the reference $CFCl_3$.

Experimental

General remarks

^{19}F NMR spectra in $CDCl_3$ were recorded on a Nicolet NT-220 spectrometer at 188.2 MHz. The chemical shifts listed in Tables 1 and 2 are in ppm upfield from $CFCl_3$. Gas chromatography was done on a Varian-6000 GC instrument equipped with a flame ionization detector. The column, 30 m capillary coated with FS-1265, a CF_3CH_2O–silicone derivative, separated the mixtures by empirical formula, if not always by individual isomers.

Preparation of 2+2 cycloadducts

We prepared the 2+2 cycloadduct of CTFE and butadiene using the method reported in the literature [3]. To obtain the highest yield based on CTFE, an excess of butadiene was used in the reaction. The cycloaddition was carried out at 150 °C/4 h and gave a crude material with ~80% cross-product and 20% vinyl cyclohexene with some cyclodimers of CTFE. Distillation gave >98% pure 2+2 cycloadduct, b.p. 110–111 °C.

One-step process

Butadiene and CTFE (5 ml min^{-1} each) were passed down a hot tube [1] containing 30 g SiC at various temperatures. The products were analyzed by on-line GC methods, and collected at −78 °C for later NMR or GC/MS analysis.

Other 2+2 cycloadducts were prepared similarly and characterized by ^{19}F NMR spectroscopy. The reactions of HFP were slower, and so were run at higher temperatures. Characterization was undertaken on crude reaction product mixtures.

Acknowledgements

We thank P. Episcopo for providing the CTFE/cyclopentadiene adducts, D. Cooke for technical assistance and K. Raffell for the many ^{19}F NMR spectra required in this work.

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