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Synthesis and aromatization of 2+2 cycloadducts of butadienes and tetrafluoroethylene*

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Abstract

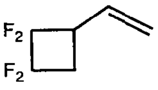
Passing tetrafluoroethylene (TFE) and hydrocarbon dienes down a hot tube at 600 °C with a contact time of a few seconds produces substituted fluorobenzenes. Specifically, tetrafluoroethylene and butadiene form 1,2-difluorobenzene. The aromatics produced by the pyrolysis of TFE and methyl-substituted butadienes do *not* necessarily result from eliminating HF from the 2+4 adducts of the starting materials.

Solid-acids such as alumina or silica/alumina accelerate the ring-expansion elimination of the 2+2 cycloadducts. Aromatic products result from the preformed 2+2 cycloadducts at temperatures 200 °C lower than the corresponding thermal reaction. The solid-acids can also influence product regiochemistry.

Introduction

Fluorocarbon and hydrocarbon olefins react in liquid-phase batch reactions to form 2+2 cycloadducts [1]. The reaction is even more facile with hydrocarbon dienes [2].

Drysdale prepared three different products from the co-pyrolysis of tetrafluoroethylene (TFE) and butadiene under various conditions [3]. Heating the two materials below 200 °C in the liquid phase produces the 2+2 adduct **1** in good yield based on TFE. The 2+2 cycloadduct rearranges to a 2+4 adduct, **2**, in a vapor-phase reaction. The reaction occurs in seconds at 500 °C or milliseconds at 600 °C. Pyrolysis at the same contact time but 100 °C hotter forms 1,2-difluorobenzene (**3**) by loss of two moles of HF [3]. The vapor-phase, continuous reaction of butadiene and TFE to give **3** in the absence of any additional reagent has been explicitly claimed in a later patent [4].



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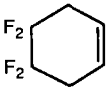

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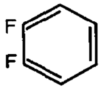

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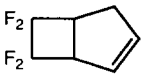
Other hydrocarbon dienes also produce adducts with TFE. The preferred route to tropolone is via the 2+2 (**4**) and 2+4 (**5**) cycloadducts of TFE and cyclopentadiene [5]. Ring-expansion of the mixture of adducts gives tetrafluorocycloheptadienes (**6**) which hydrolyze to tropolone.



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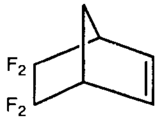

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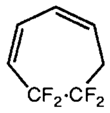

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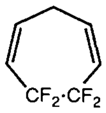


6b

Much of this work was done either before, or at the very early stages of, NMR product analyses. The limited analytical capabilities of the day gave the gross constitution of the products but often could not distinguish regiochemistry.

The purpose of this work is to characterize better the products from the aromatization of the 2+2 cycloadducts of TFE and hydrocarbon dienes. Previous papers have described work with other fluoroolefins [6] and reactions with styrenes, acrylonitrile and methyl acrylate [7].

Results

TFE and butadiene

Passing TFE and butadiene down a hot tube with a contact time of a few seconds at 400 °C gives the 2+2 cycloadduct **1**. The yield of the 2+4 adduct, 4,4,5,5-tetrafluorocyclohexene (**2**), maximizes at a low level at 500 °C. At 600 °C, the major product is 1,2-difluorobenzene (**3**). Figure 1 shows the product distribution as a function of temperature at a constant contact

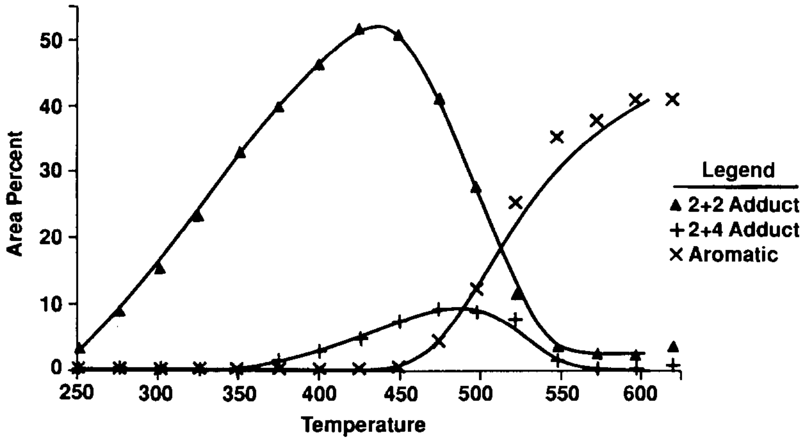


Fig. 1. Cycloadducts from butadiene and tetrafluoroethylene as a function of temperature.

time. It is possible to achieve a high yield of cyclobutane **1** but not cyclohexene **2** by this procedure.

Pyrolysis of **1** at 500 °C produces cyclohexene **2**. Pre-formed cyclobutane **1** reacted completely at 600 °C and above to give aromatic products. This temperature profile is typical for the reaction of TFE and all the substituted butadienes studied. ^{19}F NMR spectroscopy showed the liquid product at 600 °C consisted of 80 mol% **3**, 13% **2** and 6% 1,1-difluorobutadiene, the result of a 2+2 cycloreversion. The ^{19}F NMR spectrum did not show any 3,3,4,4-tetrafluorocyclohexene, an isomer of **2** expected based on Drysdale's results [5].

Passing **1** over 0.5% Pd/Al_2O_3 at 400 °C with the same contact time gave ~50% conversion to **3** with unreacted starting material as the only other component. At 450 °C, the only significant fluorine-containing product is **3**. Cyclohexene **2** never builds up as an intermediate to **3** during the pyrolysis of **1** over alumina or its derivatives.

We studied other solid-acids as accelerators for the aromatization of **1** as shown in Table 1. Palladium is not a necessary ingredient. The oxides are *reagents* rather than catalysts, and one of their functions is that of HF acceptor. HF reacts stoichiometrically with the oxide to form metal fluoride and water. A more complete list of the oxides tested and the results is available elsewhere [8]. The accelerators also affect product regiochemistry.

The one-step reaction of butadiene and TFE to **3** cannot be accelerated in the same way by solid-acids. Instead, the materials catalyze butadiene dimerization, hydrogen migration and dehydrogenation. The major liquid products from passing TFE and butadiene over alumina at 400 °C are benzene, toluene and xylenes. The catalyzed butadiene cyclodimerization must be faster than the 2+2 cycloaddition with TFE.

TABLE 1

Defluorination reagents

Reagent	Reagent weight (g)	Temperature (°C)	Yield of **3** (%)
SiC[a]	7	500	20
		550	55
NaF[a]	5	400	0
		450	1
0.5% Pd/Al_2O_3	2	400	32
6% Al_2O_3/SiO_2	2	400	25
Al_2O_3	9	350	67

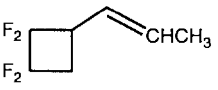
Flow rates: 1 ml h^{-1} liquid, 10 ml min^{-1} N_2.
[a]Control.

TFE and other hydrocarbon dienes

1-Methylbutadiene

Passing 1-methylbutadiene and TFE down a hot tube gave two isomeric 2+2 cycloadducts, **7**, at 400 °C. They both result from the diene reacting at the unsubstituted double bond. They differ in the *cis–trans* orientation of the methyl on the external vinyl group. A batch reaction of TFE and 1-methylbutadiene gave the same two **7** isomers.

At 600 °C, 1-methylbutadiene and TFE form methyltetrafluorocyclohexene (**8**) and a single difluorotoluene. The proton-decoupled ^{19}F NMR spectrum of the difluorotoluene exhibits an AX pattern with chemical shifts of -139.6 and -143.9 ppm, $J = 21$ Hz. This spectrum is consistent with an unsymmetrically substituted 1,2-difluorobenzene. An aromatic compound with two fluorines in a *meta* or *para* relationship would not have a 21 Hz fluorine–fluorine coupling constant [9]. Pyrolysis of **7** at 600 °C over SiC gave the same single difluorotoluene. Our GC instrument separated the two possible isomers **9** and **10**, and both analytical techniques agree that only one forms.



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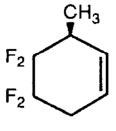

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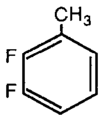

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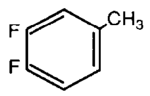


10

Initially, the structure was assigned as 2,3-difluorotoluene (**9**). This would be the expected regiochemistry from aromatization of the Diels–Alder reaction product. Subsequent studies with other methylbutadienes (see below) and more detailed NMR studies suggest that the structure of this product is actually **10**. The reaction mechanism is not as simple as we had originally thought.

Mass-spectral data cannot distinguish aromatic isomers. While GC/IR might have been able to differentiate between a 1,2,3- and 1,2,4-aromatic substitution pattern, this tool was not available to us at the time. The substituent effects of a methyl group on the chemical shift of either an *ortho* or a *para* F are too similar to distinguish the isomers unambiguously [10]. We can confidently assign the fluorine resonance at -140 ppm to the fluorine *meta* to the methyl and the one at -144 ppm to the other fluorine. However, the fluorine chemical shift and coupling constant information is still insufficient to specify the structure. We need some information relating the protons and fluorines.

The undecoupled fluorine NMR spectrum is too complex to sort out the H–F couplings because the proton spectrum is second-order even at 400 MHz. We tried an NOE experiment which irradiated the methyl group and attempted to observe an enhanced intensity at the one *ortho* fluorine. The result was ambiguous. The structure was finally assigned from the fluorine-decoupled proton spectrum shown in Fig. 2. The spectrum is an AMX system with only *one* large *ortho* H–H coupling. This result is only consistent with the 1,2,4-substitution pattern, **10**. The 1,2,3-isomer, **9**, would have a proton

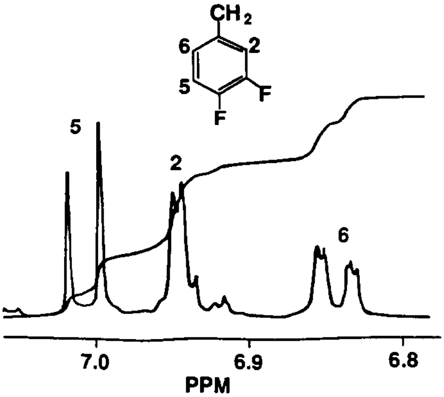


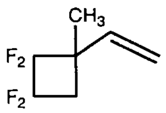
Fig. 2. Fluorine-decoupled ^1H NMR spectrum of difluorotoluene **10**.

spectrum with two large *ortho* H–H couplings. The structure of this aromatization product from 1-methylbutadiene and TFE is *3,4-difluorotoluene* **10**. This aromatization reaction does not proceed via a Diels–Alder 2 + 4 cycloadduct as the intermediate.

The aromatic product distribution is very different in the presence of solid accelerators. At 350 °C, alumina or silica/alumina produce a difluorotoluene distribution of 92% **9** and 8% **10**. The chemical shifts for the two difluorotoluenes are such that the resonances of one isomer are *between* the shifts of the other one. At higher temperatures, the fraction of **10** increases. Intramolecular methyl migration equilibrates **9** and **10** under these conditions, but we have not established the equilibrium constant.

2-Methylbutadiene

Passing 2-methylbutadiene and TFE down a hot tube at 400 °C gave 2 + 2 cycloadducts **11** and **12** in the ratio of 3:1 along with 12% of the Diels–Alder product **13**. The isomers **11** and **12** can be distinguished because **11** should have a smaller chemical shift difference between the fluorines on each CF_2 group. We obtained the same mixture of the three products by a liquid-phase cycloaddition. At 600 °C, the reaction gave both isomers of difluorotoluene. The major isomer **10** is the *same* one made from the 1-methylbutadiene cycloadduct, **7**. The minor one is its isomer, **9**.



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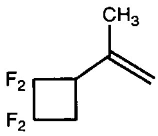

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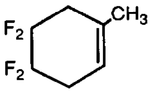

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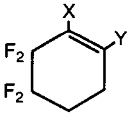


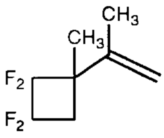
14 a) X=CH_3 Y=H
b) X=H Y=CH_3

Pyrolysis of **11** and **12** over SiC at 500 °C gave 82% conversion to a mixture of products. These included three isomeric methyl tetrafluorocyclohexenes including 10% **13**. The two new isomers produced in 10% and

4% yield both exhibited AA′XX′ fluorine spectra. This symmetry requires that the methyl be on the double bond. The possibilities for **14** have the double bond next to the fluorines and differ in the location of the methyl. The reaction also produces the two difluorotoluenes, 50% **9** and 8% **10**. Pyrolysis over alumina at 350 °C gives more difluorotoluenes than produced at 450 °C in its absence. The two isomers **9** and **10** are present in roughly equal amounts.

2,3-Dimethylbutadiene

Passing the 2 + 2 cycloadduct of 2,3-dimethylbutadiene and TFE, **15**, over SiC at 600 °C gave a mixture of two cyclohexenes **16** and **17** and one difluoroxylene. The symmetrical isomer **17** exhibits a singlet in the ^{19}F NMR spectrum while **16** shows an AA′XX′ pattern. The elimination of HF from the cyclohexenes is much slower than for either the 2-methylbutadiene or 1-methylbutadiene adducts because the cyclohexenes survive even at 600 °C. The proton-decoupled ^{19}F NMR spectrum of the difluoroxylene is a singlet at −144 ppm. Aromatization of the Diels–Alder adduct would give 4,5-dimethyl-1,2-difluorobenzene (**18**). However, the isomer 3,6-dimethyl-1,2-difluorobenzene (**19**) would also have a singlet for its proton-decoupled fluorine NMR spectrum. As for the difluorotoluenes, fluorine chemical shift arguments cannot distinguish between these two compounds.



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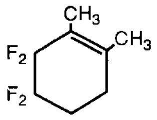

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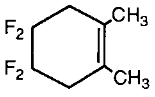

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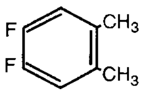

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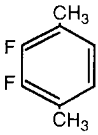

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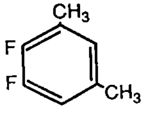
Pyrolysis of **15** over alumina at 450 °C gave three difluoroxylenes. The proton-decoupled ^{19}F NMR spectra consisted of two singlets at −142.9 ppm (40%) and −144.1 ppm (55%) and an AB pattern, $J_{FF} = 21$ Hz, at −140.6 ppm and −148.3 ppm (6%). We assign the AB pattern to 3,5-dimethyl-1,2-difluorobenzene (**20**) by additivity of the methyl effects on the fluorine chemical shifts. There are only two unsymmetrical dimethyl-1,2-difluorobenzenes. The chemical shift difference between the two fluorines should be much larger for **20** than 3,4-dimethyl-1,2-difluorobenzene (**21**). In **20** one fluorine has no *meta* methyls and the other has two, while in **21** each has one *meta* methyl.

The proton–fluorine coupling patterns allow us to assign the two symmetrical isomers. We calculate that the proton-coupled ^{19}F NMR spectrum of **18** should be a *triplet* from virtual coupling to the adjacent protons. On the other hand, the spectrum of **19** should be a *doublet* with a spacing $J_{HF} + J_{HF'}$. The peak at −144.1 ppm is basically a triplet and we assign it to **18**. The peak at −142.9 ppm is basically a doublet and we assign it to **19**. The isomer produced in the presence of SiC is 4,5-dimethyl-1,2-difluorobenzene (**18**). The reaction makes both **18** and 3,6-dimethyl-1,2-difluorobenzene (**19**) in the presence of alumina. Alumina isomerizes the difluoroxylenes, so the isomer distribution need not represent that directly formed during the aromatization. The preferred mode of aromatization results from the Diels–Alder adduct as an intermediate.

Although cyclohexene **16** is present, we did not see any 3,4-dimethyl-1,2-difluorobenzene (**21**). Instead, the unsymmetrical difluoroxylene **20** results from a single 1,2-methyl shift from either **18** or **19**.



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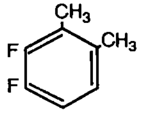

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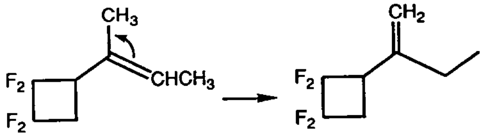
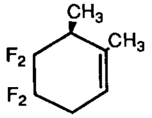
1,2-Dimethylbutadiene

The liquid-phase reaction of TFE and 1,2-dimethylbutadiene* at 150 °C/6 h gave a mixture of the 2+2 cycloadducts **22**. The ^{19}F NMR spectrum suggests that, like 1-methylbutadiene, they both have their methyls on the remaining olefin and differ in the *cis–trans* orientation about that double bond.



22a,b **23**



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Pyrolysis of **22** at 500 °C gave a rearranged vinylcyclobutane **23** and one cyclohexene. The presence of an ethyl group in **23** was confirmed by its characteristic proton NMR triplet and quartet. 2-Ethylbutadiene also forms by a 1,3-proton shift from **22** and cycloreversion. The cyclohexene does not have both methyls on the double bond because the fluorine NMR spectrum exhibits is an ABXY pattern. Cyclohexene **24** is consistent with the fluorine NMR data. There are two other possibilities with the double bond in different locations. The one with the double bond between the two methyls would have an AA'XX' spectrum. The one with an unsubstituted double bond should have *cis–trans* isomers.

The aromatic products from the pyrolysis of **22** at 600 °C include difluoroxylenes, 53% **18** and 4% **19**, and 43% difluorotoluene **10** by demethylation. The major aromatic does not result from HF elimination from the Diels–Alder product. The aromatics also include two isomers of 1,2-difluoroethylbenzene, **25** and **26**, corresponding to the difluorotoluenes produced from the 2-methylbutadiene adducts. The fluorine NMR spectra of the two 1,2-difluoroethylbenzenes **25** and **26** have a different pattern from the

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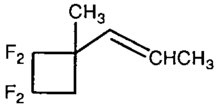
*We will name all these as substituted butadienes so that the relative positions of the methyls can be more easily compared.

corresponding difluorotoluenes **9** and **10**. Rather than an 'inside–outside pair' of resonances, the pattern for the ethyl compounds is two at low field and two at high field. We have not assigned these resonances to their respective difluoroethylbenzene isomers. The same difluoroethylbenzenes form from the pyrolysis of the 2 + 2 cycloadduct of TFE and 1,5-hexadiene.

Pyrolysis over silica/alumina gives some aromatics even at temperatures as low as 350 °C. Three of the four difluoroxylenes are significant products: 12% **18**, 45% **19** and 5% **20**. The two difluoroethylbenzenes comprise 30% and 8% of the aromatics.

1,3-Dimethylbutadiene

Heating TFE and 1,3-dimethylbutadiene in a sealed tube at 150 °C/8 h gives a 4:1 mixture of the 2 + 2 cycloadducts **27** and **28**, along with a trace of the 2 + 4 cycloadduct **29**. Pyrolysis over SiC at 450 °C gives **29** and some cycloreversion to $FC_2{=}CMeCH{=}CHMe$. Pyrolysis over SiC at 550 °C gives 83% difluoroxylene **20** and 17% cyclohexene **29**. Pyrolysis of **27** and **28** in the presence of alumina gives difluoroxylene, i.e. 94% **20**, 5% **18** and 1% **19**, and some difluorotoluenes at 400 °C.



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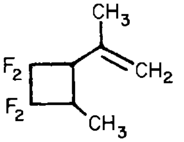

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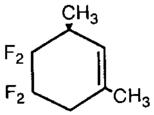

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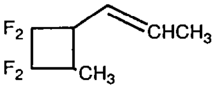
1,4-Dimethylbutadienes

A mixture of the three isomers of 1,4-dimethylbutadiene (2,4-hexadiene) reacts with TFE at 150 °C/8 h to form a mixture of four 2 + 2 cycloadducts, **30**. The *cis–trans* isomers of the methyl on the vinyl group are present in equal amounts. The *cis–trans* relationship of the ring substituents is in the ratio 7:1, but we have not determined which is which. Pyrolysis over SiC at 600 °C gave one major difluoroxylene, **19**. This product results from the aromatization of the Diels–Alder adduct. It is from this pyrolysis that we see the largest amount, but still only 3%, of 3,4-dimethyl-1,2-difluorobenzene (**21**). There was also extensive defluorination to mostly monofluorotoluene and monofluoroxylene isomers.



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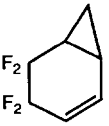


31

Cyclopentadiene

We prepared the mixture of 2 + 2 and 2 + 4 cycloadducts of cyclopentadiene and TFE, **4** and **5**, by heating cyclopentadiene and TFE in a sealed tube at 190 °C/8 h. We passed this mixture through our reactor in the presence of SiC and observed three new isomers of the starting material by GC/MS methods. The proton-decoupled ^{19}F NMR spectrum showed a pair of triplets at −104 and −112 ppm. This spectrum is consistent with a CF_2CF_2 function in a planar or rapidly equilibrating environment and a broad singlet at −103.5 ppm. The triplets are assigned to cycloheptadiene **6a** and the singlet to **6b**. In the NMR spectrum at −50 °C, the broad singlet is replaced by two broad resonances at −92 and −111 ppm, suggesting a slow ring-reversal process. The sharp triplets had broadened, but were still above any coalescence temperature.

The remaining isomer was concentrated but not purified by distillation. A combination of ^{19}F and ^{1}H NMR spectroscopy suggested the structure as tetrafluoronorcarene (**31**). The fluorine NMR spectrum shows two AB patterns with J_{FF} values characteristic of unstrained rings. The ^{1}H NMR spectrum shows several resonances in the region around 1 ppm, characteristic of cyclopropyl groups. Kinetic studies suggest **31** is the primary reaction product, but that it rapidly ring-opens to the two cycloheptadienes. Its steady-state concentration is about 5% of the total (not counting **5**). Cycloheptadiene selectivity peaks at 80% **4** conversion.

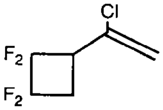
Under conditions which produce the most cycloheptadienes, norbornene **5** survives essentially intact while cyclobutane **4** reacts completely. Increasing the reaction severity to **5** does not increase the yield of **6**. Norbornene **5** decomposes under these more severe conditions to aromatic products. The maximum yield of cycloheptadiene **6** based on **4** and **5** was around 35%. This corresponds to about 65% based on the content of **4**.

In the presence of alumina, the pyrolysis of **4** and **5** occurs at lower temperature. The products are fluorobenzene and fluorotoluenes rather than cycloheptadienes **6**.

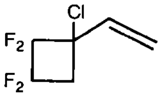
TFE and chlorinated dienes

2-Chlorobutadiene

2-Chlorobutadiene and TFE react in the liquid phase at 125 °C to give two 2+2 cycloadducts, **32** and **33**. The low-boiling major product results from reaction at the double bond containing the chlorine **33**. Our distillation was not precise enough to separate the two completely. Sufficiently different fractions were obtained to differentiate the individual behavior in the aromatization reaction.



32



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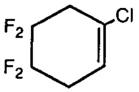

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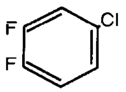

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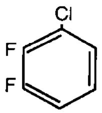


36

Passing a mixture of **32** and **33** over SiC at 600 °C gives complete conversion to three new products. One is the 2+4 adduct **34** (29%) and the other two are 1,2-difluorochlorobenzenes by the AX coupling patterns, $J_{FF}=21$ Hz. The problem of identifying the two possible isomers of $C_6H_3F_2Cl$

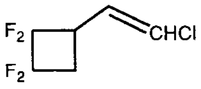
is the same as that encountered with the methyl derivatives. We assign the products by analogy with those results. The 'outer' AX doublet (42%) is assigned the 1,2,4-structure **35**, while the inner doublet (23%) is assigned the 1,2,3-structure **36**. The ratio of the two isomers is the same from alumina at 400 °C. In contrast, passing enriched **33** over either SiC at 600 °C or silica/alumina at 450 °C gave 85% **35** and 5% **36**.

1-Chlorobutadiene

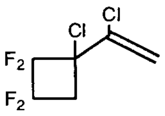
1-Chlorobutadiene and TFE react in the liquid phase at 125 °C to give two isomers of the 2+2 adduct, **37**. By analogy with 1-methylbutadiene, they seem to have an external HC=CHCl with both *cis* and *trans* configurations. At 350 °C, ring-expansion over alumina gives a low conversion to three aromatic products. GC/MS and ^{19}F NMR analyses identified the products as the 1,2-difluorobenzene **5** (10%) and the two isomers of 1,2-difluorochlorobenzene. The ratio of **35** to **36** is 1:8. The pyrolysis products from SiC at higher temperatures were too complex to analyze.

2,3-Dichlorobutadiene

We prepared the 2+2 adduct of TFE and 2,3-dichlorobutadiene, **38**, by heating the two starting materials at 150 °C. Pyrolysis of **38** gave mostly the 2+4 adduct **39** at 550 °C along with minor amounts of a mixture of fluorochlorobenzenes.



37a,b



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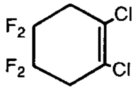

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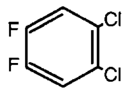


40

The aromatic product produced in the presence of alumina at 450 °C is assigned the structure 4,5-dichloro-1,2-difluorobenzene (**40**). The undecoupled proton (7.33 ppm) and fluorine NMR spectra are both deceptively simple triplets, $J=9$ Hz. The fluorine chemical shift of −136.7 ppm does not distinguish between the isomeric possibilities. The definitive structure proof of **40** came from the carbon NMR spectrum. There are three types of carbon in the molecule, only one of which has a directly bonded proton. The chemical shift for carbons bearing fluorine is 148.9 ppm, $J_{CF}=254$ Hz, $J_{CCF}=15$ Hz. The chemical shift for carbons bearing chlorine is 125.5 ppm, doublet, $J=5$ Hz. The chemical shift of the carbon bearing a directly-bonded proton is 119.1 ppm. This signal is the most intense in a proton-decoupled spectrum because of the Overhauser effect. The resonance is an X part of an ABX multiplet with the sum of the AX and BX coupling constants being >20 Hz. This coupling pattern is consistent with **40**, because it contains the fragment –HC=CF–CF=, but not with the alternative 3,6-dichloro-1,2-difluorobenzene (**41**).

Discussion

Mechanism of cycloadduct aromatization

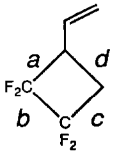
The regiospecificity of some of the aromatic products from the ring-expansion of the 2+2 cycloadducts of methyl-substituted butadienes is unexpected. The bond which breaks in the ring-expansion reaction is *not always* the single bond formed in the previous cycloaddition. Rather it may be the sigma portion of the original double bond of the diene.

There are analogies which may be useful in thinking about these results. Pyrolysis of the 2+2 cycloadduct of C_2F_4 and C_2H_4 gives $H_2C{=}CF_2$ [11]. The two carbons of TFE end up in separate molecules in the products. The bonds which formed in the cycloaddition are not the ones which break in the cycloreversion. Thermodynamically, two $F_2C{=}CH_2$ molecules are more stable than one each of TFE and ethylene. The major product of the Diels–Alder dimerization of $H_2C{=}CF{-}CH{=}CH_2$ results from the intermediate allyl radicals with fluorine at the node [12]. Terminal fluorine does not stabilize an allylic radical.

We have not been able to postulate a single, simple mechanism which explains all our experimental facts. The best mechanisms explain most of the facts, but with a few pesky outliers. Of course, there is no reason to assume that all the reactions studied here proceed by exactly the same mechanism. We will use the straw-man approach to postulate, and then disprove, some potential mechanisms. These initially appeared plausible, but proved not to be in accord with the results of further experiments.

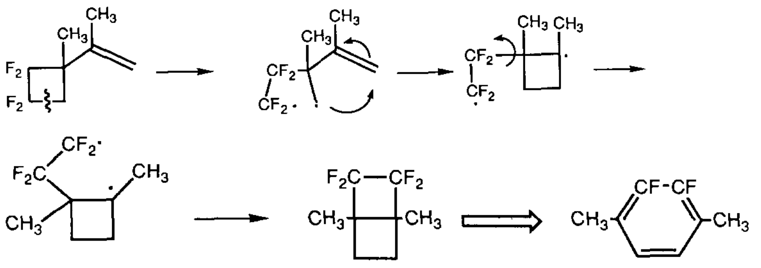
The first aromatization mechanism we considered involves the 2+4 Diels–Alder adducts as the key intermediates. This mechanism predicts **9** as the aromatic product from 1-methylbutadiene and TFE, not the observed product which is **10**. Many of the 2+2 cycloadducts of methylbutadienes and TFE thermally produce 1,2-difluoromethylbenzene isomers, inconsistent with this mechanism.

There are four non-equivalent cyclobutane bonds in the 1,1,2,2-tetrafluoro-3-vinylcyclobutanes. Bonds *a* and *c* formed in the 2+2 cycloaddition. Bonds *b* and *d* are the sigma portions of the initial double bonds. Breaking bond *a* and reclosing at the terminus of the allylic hydrocarbon radical forms the Diels–Alder 2+4 cycloadduct. Breaking bond *b* would lead to products in which the two fluorines become separated, inconsistent with the observed products. Breaking bond *c* is not productive in most cases. Breaking bond *d* and reclosing at the other end of the allylic radical predicts many of the observed aromatic products.



Bond strength considerations allow us to predict which bond will break. The bond strengths of the carbon–carbon single bonds in ethane, 1,1,1-trifluoroethane and hexafluoroethane are 89, 101 and 99 kcal mol^{-1} [13]. The weakest bond is in ethane, and we would predict that bond *d* would break in the cyclobutanes.

The two difluoroxylene isomers **19** and **21** from 1,4-dimethylbutadiene are consistent with breaking bonds *a* and *d*. This scheme explains the formation of **10** from 1-methylbutadiene, but is insufficient to explain **19** from 2,3-dimethylbutadiene. A possible mechanism to get to **19** may involve first breaking bond *c* in the generalized structure. The $CH_2\cdot$ radical might add across the double bond to form a new cyclobutyl radical. A second ring closure leads to a bicyclohexane **42**. Compound **42** has no easy way of eliminating HF. Since HF elimination is an obligatory step to aromatics, unusual modes must be postulated. 1,3 HF elimination to a Landenberg benzene followed by valence tautomerization to the benzene would give the observed difluoroxylene isomer, **19**. Several steps may be concerted.



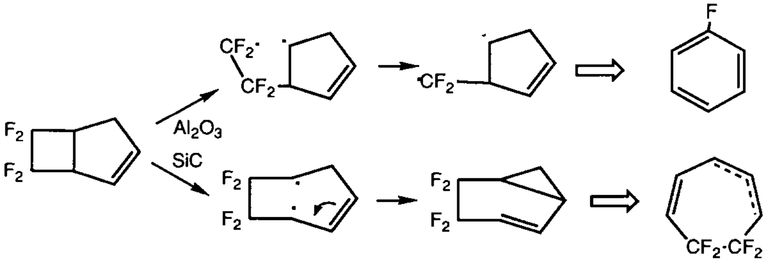
42

Some of the cyclohexenes seen are *not* the intermediates to the aromatics eventually formed. These cyclohexenes must aromatize either via free olefin and diene or at least back through the original 2 + 2 adducts. An alternate ring-expansion through other, undetected six-membered ring intermediates eventually gives the aromatics observed. Suppose the olefins and the four- or six-membered rings were in equilibrium. The aromatic isomer formed might be quite unpredictable based on the stabilities of the observed intermediates. Alternatively, the aromatic isomers might equilibrate after they formed. It is unlikely that the differences in the free energies of the aromatic products are the origin of the isomer distribution.

Accelerator directivity

The regiochemistry of some ring-expansion products is influenced by the presence of an inorganic accelerator. Passing **7** over alumina or silica/alumina versus SiC gives different difluorotoluene isomers as the major product. Bond *d* breaks with SiC; bond *a* is the primary cleavage site with alumina.

The cyclopentadiene–TFE adducts extrude difluorocarbene in the presence of solid-acids. The new diradical is the equivalent of the product of cyclopentadiene and $CHClF_2$, which ring-expands and aromatizes to fluorobenzene [4]. Radicals with $CF_2CF_2\cdot$ ends depolymerize, at least in part, by extruding difluorocarbene [15].



Polar solids may stabilize the normally less-favored diradical by ionic interactions. The mechanism then proceeds in an analogous manner to the thermal one.

Experimental

Caution: TFE is a thermally unstable compound which can exothermically decompose to CF_4 and carbon. The cylinders we used never contained more than 50 g of the material and were designed to contain an instantaneous decomposition without rupturing.

General remarks

^{19}F NMR spectra in $CDCl_3$ were recorded on a Nicolet NT-220 spectrometer at 188.2 MHz. Chemical shifts are reported in ppm *upfield* from $CFCl_3$. Unless otherwise specified, all spectra were obtained with broad-band proton decoupling. Gas chromatography was undertaken on a Varian 6000 GC instrument equipped with a flame ionization detector. The column, a 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. The alumina used was Harshaw AL-0104. The silica/alumina was Harshaw AL-1602, 91% SiO_2/Al_2O_3.

^{19}F NMR spectra generalities

The proton-decoupled ^{19}F NMR spectra of all 2 + 2 cycloadducts were ABXY types. The geminal coupling constants were characteristically about 200 Hz. The patterns for the 2 + 4 cycloadducts were either ABXY or AA'XX' depending on whether either of the two other sp^3 carbons had two different substituents. When the geminal coupling could be measured, it was in the range 260–280 Hz. The vicinal couplings did not aid in structure identification. The spectra of aromatic compounds were either A_2 or AX patterns. Relative to the parent compound, each methyl group in either the *ortho* or *para* position shifts a fluorine resonance upfield by about 5 ppm. To a first approximation, *meta* methyl substitution has no effect on the chemical shift. These general rules, and the change in concentration of the reaction products

TABLE 2

^{19}F NMR parameters for 2 + 2 cycloadducts

Compound	δ_1 (ppm)	δ_2 (ppm)	J_1 (*Hz*)	J_2 (Hz)	Compound	δ_1 (ppm)	δ_2 (ppm)	J_1 (*Hz*)	J_2 (Hz)
1	110.2	111.2	206	209	**28**	109.2	111.1	205	208
	129.7	118.9				130.1	119.6		
4	109	115	209	209	**30a**	133.1	133.3	207	207
	125	118				109.4	110.4		
7a	109.4	119.4	205	205	**30b**	135.5	135.7	207	207
	111.1	129.5				112.1	112.3		
7b	110.5	119.4	205	205	**30c**	124.2	124.9	209	209
	111.4	130.0				115.2	115.4		
11	111.4	122.0	211	204	**30d**	126.9	127.6	209	209
	113.1	124.7				110.7	112.2		
12	110.8	107.3	208	202	**32**	108.1	110.8	204	209
	120.3	132.4				131.3	119.6		
15	109.4	118.0	210	205	**33**	111.7	115.8	213	199
	115.5	127.7				113.7	121.6		
22a	132.9	120.4	203	208	**37a**	111.1	109.4	206	209
	107.2	110.9				118.8	128.5		
22b	130.1	120.3	205	207	**37b**	111.1	109.9	206	209
	?	?				119.2	129.0		
23	107.1	110.5[a]	201	201	**38**	110.3	112.1	212	200
	120.7	132.5[a]				114.0	124.3		
27	111.3	122.0	209	203					
	113.1	124.6							

[a] Partners may be reversed.

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

as a function of severity, sufficed to place most of the resonances in one of the three product categories.

Preparation of 2 + 2 cycloadducts

We prepared the 2 + 2 cycloadduct of TFE and butadiene by the literature method [2]. To obtain the highest yield based on TFE, 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% vinylcyclohexene. Distillation gave > 98% pure 2 + 2 cycloadduct, b.p. 82 °C.

Syntheses

We prepared the other 2 + 2 cycloadducts by heating 50 g TFE and a slight deficiency of hydrocarbon dienes in sealed tubes at the temperatures given in the Results section. The major ^{19}F NMR parameters of the 2 + 2 adducts are given in Table 2, those for the 2 + 4 adducts in Table 3 and for the aromatic products in Table 4.

TABLE 3

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

Compound	δ_{12} (ppm)	δ_{34} (ppm)	J_{12} (*Hz*)	J_{34} (Hz)
2	120.2	120.2		
5	109 125	115 118	209	209
8	115.5 123.1	129.6 129.6	253	–
13	120.0	121.6	–	–
14a	107.1	118.4	–	–
14b	114.2	121.6	–	–
16	120.2		–	–
17	112.2	115.4	–	–
24	117.6 121.5	125.7 129.2	252	253
29	115.2 123.2	130.4 131.7	253	259
31	92.2 115.3	99.7 122.5	283	258
34	119.3	121.8	–	–
39	120.2		–	–

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

TABLE 4

^{19}F NMR chemical shifts for substituted fluorobenzenes

Compound	Shifts (ppm)		Compound	Shifts (ppm)	
3	138.9	–	**21**	143.4	143.8
9	140.0	143.5	**25**	139.3	143.4
10	139.6	143.9	**26**	139.8	145.4
18	144.1	–	**34**	135.1	140.3
19	142.9	–	**35**	135.4	139.2
20	140.6	148.3			

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

One-step process

C_4H_6 and TFE (5 ml min^{-1} each) were passed down a hot tube (see below) containing 30 g SiC at temperatures between 400 and 600 °C. The products were analyzed by on-line GC and collected for later NMR analysis.

Pyrolysis of 2+2 cycloadducts

A liquid flow of 1 ml h^{-1} vinylcyclobutane and a gas flow of 5 ml min^{-1} N_2 were passed through a 3/4″×5″ Vycor tube filled with 10 g solid. With SiC at 400 °C, generally the starting materials survived unchanged; at 500 °C, the ring-expanded cyclohexenes were the major products. At 600 °C, loss of 2HX gave aromatic products. In the presence of polar solids, aromatics were the major products at temperatures as low as 450 °C, and cyclohexenes were never seen.

All analytical work and product identification was undertaken on crude mixtures obtained directly from the reactors.

Acknowledgements

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References

1 J. D. Roberts and C. M. Sharts, *Org. React.*, *12* (1975) 1; W. H. Sharkey, *Fluorine Chem. Rev.*, *2* (1968) 1.
2 D. D. Coffman, P. L. Barrick, R. D. Cramer and M. S. Raasch, *J. Am. Chem. Soc.*, *71* (1949) 490.
3 J. J. Drysdale, *US Pat. 2 861 095* (1958).
4 O. M. Nefedov, U. Shukhova and A. A. Ivashenko, *US Pat. 3 499 942* (1970).
5 J. J. Drysdale, W. W. Gilbert, H. K. Sinclair and W. H. Sharkey, *J. Am. Chem. Soc.*, *80* (1958) 3672.
6 F. J. Weigert and R. F. Davis, *J. Fluorine Chem.*, *63* (1993) 59.
7 F. J. Weigert, *J. Fluorine Chem.*, *63* (1993) 53.
8 F. J. Weigert, *US Pat. 4 754 084* (1988).
9 J. W. Emsley, J. Feeney and L. H. Sutcliffe, *High Resolution Nuclear Magnetic Resonance Spectroscopy*, Pergamon Press, Oxford, 1966.
10 H. S. Gutowsky, D. W. McCall, B. R. McGarvey and L. H. Meyer, *J. Am. Chem. Soc.*, *74* (1952) 4809.
11 R. T. Conlin and H. M. Frey, *J. Chem. Soc., Faraday Trans. 1*, *76* (1980) 322.
12 F. J. Weigert, *J. Org. Chem.*, *42* (1977) 3859.
13 D. Griller, J. M. Kanabus-Kaminska and A. Maccol, *J. Mol. Struct.*, *163* (1988) 125.
14 L. A. Errede, *J. Org. Chem.*, *27* (1962) 3425.