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Pyrolysis of cyclobutanes from styrenes, acrylonitrile and methyl acrylate and polyfluoroolefins*

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Abstract

The 2+2 cycloadduct of styrene and TFE (**1**) ring-expands and eliminates HF like a *butadiene* adduct to give 2,3-difluoronaphthalene (**3**). Cyclobutane **1** also cleaves to styrene and 1,1-difluorostyrene. Titania and other solid-acids accelerate the ring-expansion reaction and direct the ring expansion toward 1,2-difluoronaphthalene (**4**).

The cycloadduct of TFE and acrylonitrile **11** eliminates HF to form cyclobutene **12** and the isomeric butadiene **13**. Pyrolysis at even higher temperatures gives low yields of tetrafluorobenzonitrile (**15**). Methyl acrylate behaves like acrylonitrile, but the reactions are slower and the products less stable.

Introduction

Tetrafluoroethylene (TFE), chlorotrifluoroethylene (CTFE) and other 1,1-difluoroolefins thermally form 2+2 cycloadducts with hydrocarbon olefins and dienes [1]. Pyrolysis of these cyclobutanes gives different products depending on the hydrocarbon half of the molecule. For example, pyrolysis of the adduct of TFE and ethene gives two moles of vinylidene fluoride [2]. The adducts of TFE and hydrocarbon *dienes* such as butadiene ring-expand to form tetrafluorocyclohexenes, and ultimately 1,2-difluorobenzenes [3]. Adducts with acetylenes ring-open to give tetrafluorobutadienes [4].

In the accompanying papers, we describe work on the ring-expansion reactions of TFE and hydrocarbon dienes [5], and other (polyfluoro)olefins [6]. We present here our studies on the pyrolysis of the TFE and CTFE 2+2 adducts with styrenes, acrylonitrile and methyl acrylate.

Results

Styrenes

Passing styrene and TFE down a hot tube filled with SiC at 300 °C or heating the two in a shaker tube at 175 °C produces the 2+2 cycloadduct **1**. At 600 °C, pyrolysis of either **1** or the two olefins gives three products. We used GC/MS to establish the molecular formulas and ^{19}F NMR spectroscopy to identify the particular isomers. The first product is the result of a 2+2

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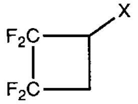
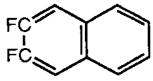
cycloreversion, $F_2C{=}CHC_6H_5$ (**2**). The $CH_2{=}CF_2$ presumably also formed was not identified. The other two products are *naphthalenes.*

The major naphthalene isomer is 2,3-difluoronaphthalene (**3**). The minor isomer is 1,2-difluoronaphthalene (**4**). If we assume that the two fluorines remain *ortho*, the structures follow simply from the presence of fluorine–fluorine coupling in **4** and its absence in **3**. There are no products analogous to the cyclohexenes from dienes.



1 X = C_6H_5
11 X = CN
17 X = COOMe



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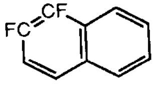

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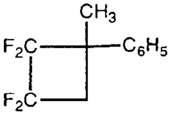
Solid-acids such as alumina or zirconia accelerate the ring-expansion of **1**. At low temperatures the major naphthalene is **4**, while at high temperatures the major product is **3**. At low temperatures, under identical conditions, *without* any solid-acid, cyclobutane **1** remains unreacted.

Passing α-methylstyrene and TFE down a hot tube produces cyclobutane **5** at 400 °C. At 600 °C, the product consists of the cracking product $F_2C{=}C(Me)C_6H_5$ (**6**) (58%), and ring-expansion products 1-methyl-2,3-difluoronaphthalene (37%) (**7**), and 1-methyl-3,4-difluoronaphthalene (5%) (**8**). The structures of the methyl difluoronaphthalenes follow from their ^{19}F NMR spectra.



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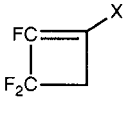


10 X = C_6H_5
12 X = CN
18 X = $COOCH_3$

CTFE and styrene form two isomers of the 2+2 cycloadduct **9** when heated at 120 °C for 1 d. Ring expansion to difluoronaphthalenes occurs, but the yields are much poorer than with **1**. The major product from passing **9** over 86% titania/14% alumina is temperature-dependent. At 400 °C, the only naphthalene is the 1,2-isomer **4**, while at 500 °C the ratio of **4** to **3** is 1.8.

Both the styrene–TFE adduct **1** and the styrene–CTFE adduct **9** eliminate HX to produce the same trifluorocyclobutene **10** in the presence of refluxing Bu_3N. HCl elimination from **9** is much faster than HF elimination from **1**.

Acrylonitrile

The 2+2 cycloadduct of TFE and acrylonitrile **11** [7] slowly eliminates HF at 450 °C to form cyclobutene **12** (50%), the isomeric butadiene $F_2C{=}CFC(CN){=}CH_2$ (**13**) (42%) and the isomeric cyclobutene **14** (8%). Pyrolysis at 700 °C gives low yields of a tetrafluorobenzonitrile, (C_7HF_4N), identified by GC/MS methods. ^{19}F NMR chemical shift additivity considerations identified the specific isomer as **15**. A minor product is 1,2,3-trifluoro-5-

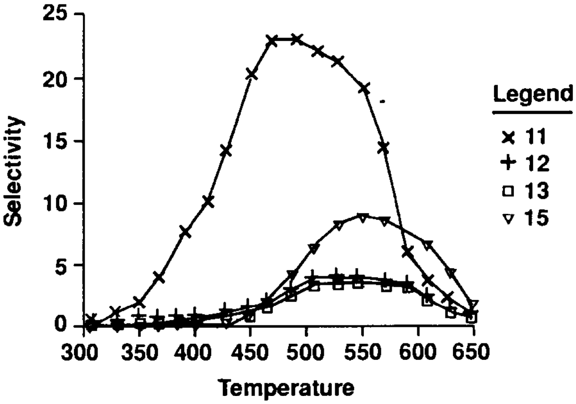


Fig. 1. Products from the reaction of acrylonitrile and tetrafluoroethylene as a function of temperature.

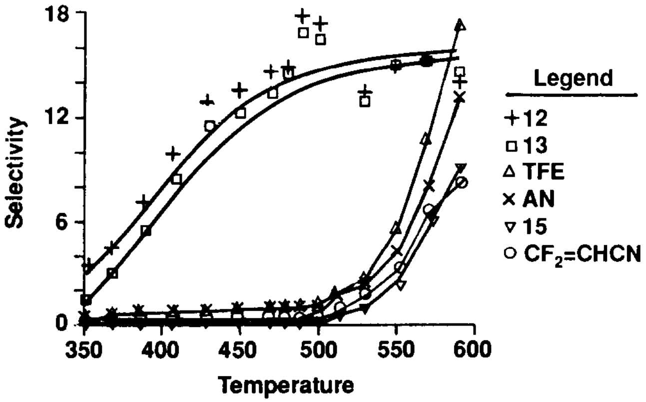
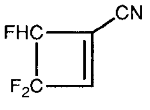


Fig. 2. Products from the reaction of cyanocyclobutane **11** as a function of temperature.

cyanobenzene, also identified by a combination of GC/MS and ^{19}F NMR methods. The total recovery is not good. Formally, aromatization must involve the loss of two fluorine atoms, a much more difficult process than the elimination of HF.



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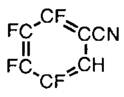

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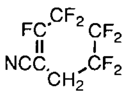

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Figure 1 shows the products from passing TFE and acrylonitrile through our hot tube as a function of temperature. Cyclobutane **11** is the major product up to 450 °C. Cyclobutene **12** and diene **13** are never major products, but form in apparently parallel processes. Benzonitrile **15** peaks, but is still a minor product, at 550 °C before extensive cracking takes over.

Figure 2 shows the products from the pyrolysis of cyclobutane **11** as a function of temperature. Up to 500 °C, HF elimination products, cyclobutene **12** and diene **13**, form in nearly quantitative yield at modest conversion. At higher temperatures, cycloreversion to TFE and acrylonitrile, cycloreversion to $F_2C{=}CHCN$ and aromatization take place, and the total recovery decreases.

Pyrolysis of **11** in the presence of excess TFE at 550 °C gives two new products with $m/e = 246$ ($C_{10}H_3F_5N_2$) and $m/e = 233$ ($C_7F_7H_2N$). The first is formally a dimer of either **12** or **13** with the loss of one molecule of HF. The specific structure is unknown. The second is consistent with cyclohexene **16** with its plane of symmetry. There are no fluorines in the NMR spectrum with the large J_{FF} value expected for non-equivalent fluorines in a six-membered ring.

Passing cyclobutane **11** over alumina at 300 °C produces 38% cyclobutene **12** as the sole product. At 350 °C, the effluent is 52% **12** and 9% butadiene **13**. Above 400 °C, little organic product survives. Carbon and titania also accelerate HF elimination to give **12** but are less effective than alumina.

Methyl acrylate

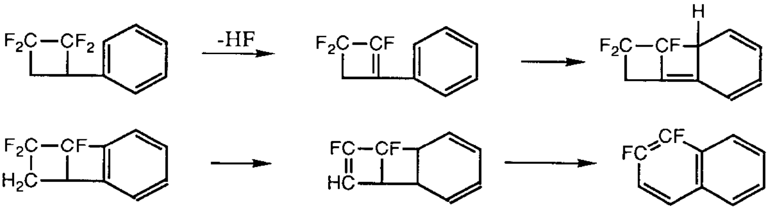
The 2+2 cycloadduct of TFE and methyl acrylate **17** forms both cyclobutene **18** and diene $F_2C{=}CFC(COOCH_3){=}CH_2$ (**19**) when pyrolyzed over SiC at 550 °C. The reaction is much slower than its acrylonitrile analog, and conversions above 20% could not be achieved without significant cracking. We did not see the analogous cyclohexene or tetrafluoromethylbenzoate at pyrolysis temperatures up to 600 °C.

Alumina promotes the elimination of HF from **17**. At 250 °C a significant conversion to cyclobutene **18** occurs, but at higher temperatures extensive cracking took place with no improvement in the cyclobutene yield. Refluxing **17** with dry KF produces cyclobutene **18** slowly, but cleanly.

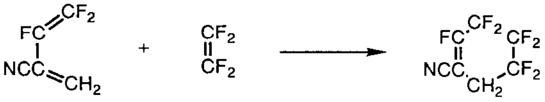
Discussion

2+2 Adducts of styrenes and TFE ring-expand in a reaction similar to that observed in the 2+2 adducts of TFE and butadienes [5]. One double bond of styrene's benzene ring behaves like an olefin in this reaction.

Alternatively, alumina may first promote HF elimination to form a cyclobutene. This cyclobutene now has several options. Styrene derivatives valence-tautomerize, including one of the double bonds of the aromatic ring, to the observed difluoronaphthalene isomer.



A mechanism to form **15** might involve cycloaddition of TFE to either double bond in butadiene **13** followed by ring-expansion of the vinylcyclobutane to give the cyclohexene. Alternatively, TFE could react directly with **13** via a 2+4 addition to give cyclohexene **16**. In either case, this is a rare example of building a six-membered ring from three olefins. This cyclohexene can aromatize to produce polyfluorobenzonitriles by the loss of two fluorine atoms. This mechanistically difficult transformation may account for the low yields of polyfluorobenzonitriles by this process.



Experimental

General remarks

The experimental apparatus has been described elsewhere [8].

^{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

TABLE 1

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

Compound	Fluorine shifts of AB portion (ppm)	J_{AB} (Hz)	Fluorine shifts of X portion (ppm)
1	−105.8 −128.9	202	
	−108.8 −118.9	208	
5	−109.2 −115.2	210	
	−117.6 −123.0	202	
9	−108.1 −109.3	199	137.1
	−99.1 −119.5	193	108.7
17	−108.7 −110.1	208	
	−117.4 −124.7	208	

TABLE 2

^{19}F NMR data for cyclobutenes

Compound	Fluorine shifts (ppm)	
	A_2	X
10	−110.9	−112.4
12	−114	−84
14	−110.8	−191.5
18	−114.8	−92.4

TABLE 3

^{19}F NMR data for difluoronaphthalenes

Compound	Fluorine shifts (ppm)
3	−137.8 (t, 5)
4	−142.0 (ddd, 19, 10, 5); −154.9 (dd, 19, 6)
7	−137.8 (dd, 21, 11); −140.6 (ddq, 21, 5, 2.5)
8	−142.9 (dd, 19, 11); −154.0 (dd, 19, 7.5)

TABLE 4

^{19}F NMR data for 1,1-difluoroolefins

Compound		Fluorine shifts (ppm)	
		AB	X
2	−84.8 (dd, 31, 4)	−82.9 (dd, 31, 26)	
6	−91.0 (dd, 44, 3)	−91.4 (dd, 44, 3)	
13	−178.5	−95	−108
19	−113.5 (d, d, 114, 64)	−99.5 (d, d, 31, 64)	−171.7 (d, d, 114, 31)

instrument equipped with a flame ionization detector. The column was a 30 m capillary coated with FS-1265, a CF_3CH_2O–silicone derivative.

Table 1 contains the ^{19}F NMR data for the cyclobutanes, Table 2 for the cyclobutenes, Table 3 for the difluoronaphthalenes and Table 4 for the 1,1-difluoroolefins as obtained in this work.

Characterization was undertaken on crude reaction mixtures.

Acknowledgement

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