Journal of Fluorine Chemistry, 52 (1991) 125–131

Received: July 27, 1990; accepted: November 24, 1990

THE THERMAL CYCLOADDITION OF PERFLUORO-1,3-BUTADIENE WITH BUTA-1,3-DIENE

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SUMMARY

The major products from the cross-dimerization of butadiene and perfluorobutadiene are a 2+2-cycloadduct and a 2+4-cycloadduct. Perfluorobutadiene is the diene and butadiene is the dienophile.

Minor products include the 4+4-cycloadduct, a criss-cross product, and several others containing fluorine on four membered rings. Pyrolysis converts both the 2+2- and the 2+4-adducts to the criss-cross product. Pyrolysis of the 2+2-adduct in the presence of carbon also gives 1,2,3- and 1,2,4-trifluorobenzenes.

The fluorine nmr data for C_4F_6 cycloadducts helps assigning the structures.

INTRODUCTION

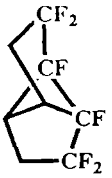
The dimerizations of substituted 1,3-dienes have played an important role in our understanding of pericyclic reactions [1]. Butadiene, the parent of the group, gives mainly the 2+4-cycloadduct, 4-vinylcyclohexene. Careful study of the product mixture revealed the presence of tiny amounts of 2+2- and 4+4-cycloadducts [2].

The dimerization of perfluorobutadiene is less well understood. Miller first studied the reaction nearly 40 years ago [3]. This was long before the powerful analytical tools we take for granted today were discovered. He distilled the products and was able to separate a dimer and a trimer fraction. He characterized (incorrectly) only one crystalline dimer as a double 2+2-cycloadduct, the perfluoro-analog of structure 5. Later an X-ray crystal structure showed that it was actually 11, the criss-cross isomer of Miller's postulated structure [4].

Compounds with the formula $C_8H_6F_6$ can also be formed by 1,1,2-trifluorobutadiene dimerization [5]. The major isomers are

2+4-cycloadducts with both halves of the diene adopting the roles of diene and dienophile. Small amounts of 4+4-cycloadduct also form. As for the perfluorobutadiene dimerization, one fraction crystallized. An X-ray structure showed that this fraction also was a criss-cross dimer 1.

The reaction of butadiene and perfluorobutadiene has been reported [6]. The two major products were correctly identified as the 2+2-cycloadduct 2 and the 2+4-cycloadduct 3. This paper dealt mainly with the synthetic aspects of the cycloadducts of perfluorobutadiene and not with minor products and mechanism.



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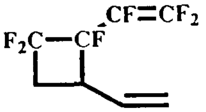

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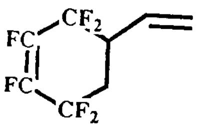

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We have been interested in the 2+2-cycloadditions of fluoroolefins and hydrocarbon dienes [7]. Ring expansion of these vinylcyclobutanes leads initially to cyclohexenes. The four-membered ring enlarges to a cyclohexene and eventually gives substituted fluorobenzenes by elimination of HF. The 2+2-cycloadduct 2 could potentially ring expand via either vinyl group.

This paper describes further cross-dimers of C_4H_6 and C_4F_6 and the ^{19}F-nmr spectra used to identify the subtle differences between the numerous isomers. For comparison, we also report nmr characterization of the dimers of C_4F_6 first reported by Miller [3]. Unexpectedly, pyrolysis of the 2+2-cycloadduct 2 does not give any cyclohexene products.

RESULTS

Products from Butadiene and Perfluorobutadiene

Mixtures of 2g butadiene and 3g perfluorobutadiene and 0.1g hydroquinone were condensed into stainless steel reaction vessels and heated for the times and temperatures in Table 1.

TABLE 1

Reaction Conditions and NMR Isomer Distributions of C_4F_6/C_4H_6 Adducts

Temp °C	Time Hr	Mole % 2	3	4	1
125	8	56	41	3	2
150	8	53	30	5	13
175	4	39	30	8	23

The yields in Table 1 were determined by integrating the F-19 nmr spectra of the unpurified reaction products.

Cross-dimers did not form when the two dienes were passed down a hot tube filled with SiC. The only product was vinylcyclohexene from butadiene dimerization.

The low boiling fractions from the reaction of C_4H_6 and C_4F_6, bp 97-118 C, contained 4-vinylcyclohexene and only one fluorinated compound, the criss-cross dimer 1. None of the other primary products could be completely purified by distillation. We continued our nmr studies on fractions enriched to different extents in the various isomers.

Structure Identification

The fluorine nmr spectrum of the major product 2 showed six different fluorines. They are distributed as a CF_2=CF- group, a CF_2 with non-equivalent fluorines in a four-membered ring, and a tertiary fluorine. There are two possible 2+2-cycloadducts with structure 2, differing by the *cis* and *trans* ring juncture. Only one was present and we have not been able to assign its stereochemistry.

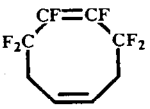
The other major primary product 3 also had six different fluorine resonances. This compound has no resonances attributable to a -CF=CF_2 group. Instead, there are two different CF_2 groups. By the geminal coupling constants of 272 and 285 Hz, both are assigned to a six membered ring. The two remaining fluorines are on olefinic carbons. Their coupling constant is consistent with a *cis* ring geometry. This isomer is the Diels-Alder structure 3. The isomeric 2+4-cycloadduct with C_4F_6 as the dieneophile would have a CF_2=CF- group, and is not present.

The nmr spectrum of the criss-cross adduct 1 was identical to that of the product obtained earlier from the dimerization of

1,1,2-trifluorobutadiene [5]. As the severity of the reaction increases, the criss-cross dimer 1 grows at the expense of 2 and 3. Thus it is a secondary, and not a primary cycloaddition product.

The 4+4-cycloadduct, 4, can also be detected though it is never present to a large extent. It has a distinctive AA'XX'AA' coupling pattern. The chemical shifts are very similar to those previously assigned to the 4+4-cycloadduct of CF_2=CFCH=CH_2 [6].

One intermediate fraction contained additional minor components. There are CF_2 groups which may be assigned to four membered rings according to the geminal coupling constant. There are also tertiary fluorines assigned by their high field resonances. There are **SIX** additional cycloadducts to which these peaks might be assigned. They are the syn and anti isomers of [2.2.0.0]tricyclooctane 5, two isomers of tricyclo[3.1.1.$1^{2,4}$]-octane 6 and two isomers of tricyclo[4.1.1.$0^{3,6}$]octane 7. At present we cannot complete the assignment.



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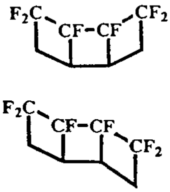

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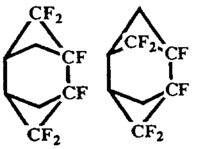

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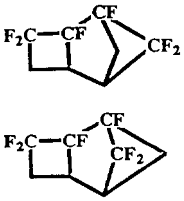

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Table 2 gives the assignments of fluorine nmr spectra for the products from the reaction of C_4F_6 and C_4H_6.

Secondary Products

The mixture obtained at 150° was reheated for 8 hrs at the same temperature. The 2+2-cycloadduct 2 decreased, and the criss-cross product 1 increased.

The 2+2-cycloadduct 2 was passed down a hot tube filled with SiC at 400° and a contact time of a few seconds. The only product isolated was criss-cross dimer 1. There was no ring expansion to a cyclohexene like that observed for the cycloadducts of TFE and butadiene [8].

The rearrangement of 2 to 1 occurred at significantly lower temperatures when activated carbon replaced the SiC in the reactor. Carbon is known to catalyze radical reactions [9]. At higher temperatures, and only in the presence of carbon, two new products were observed. GC/MS and nmr identified the products as 1,2,3- and 1,2,4-trifluorobenzene.

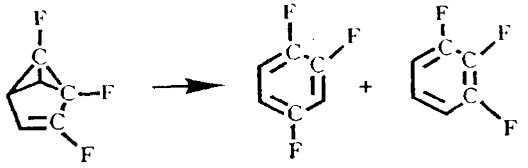
From the studies under more severe conditions, both the 2+2- and 2+4-cycloadducts are primary products of the cycloaddition. Cyclooctadiene 4 and criss-cross adduct 1 are secondary products derived from thermolysis of the primary products.

TABLE 2

Fluorine NMR Data for C_4F_6/C_4H_6 Cycloadducts

Compound	Assignment	Chemical Shift	Pattern	J
1	CF_2	109.9	d,m	228
	CF_2	112.5	d,m	228
	CF	195.3	m	
2	=CF	94.0	d,d,d	61,35,6
	=CF	111.2	d,d,d,t	115,61,18,5
	=CF	186.2	d,d,d,t	115,35,24,2
	CF	180.0	d,d,d,d,d	24,17,12,6,3
	CF_2	104.4	d,d,d,d	205,12,4,2
	CF_2	113.0	d,d	205,3
3	CF_2CVi	93.2	d,d	272,10
	CF_2CVi	100.4	d,d	272,30
	CF_2CH_2	86.5	d,br	285
	CF_2CH_2	87.7	d,br	285
	=CF	144.1	t,t	18,12
	=CF	167.2	d,d,d	23,10,5
4	=CF	146.5	m	
	CF_2	92.0	(q)	
5, 6, 7	(Assignment unknown)			
	CF_2	97.1	d,d,d	211,24,5
	CF_2	107.6	d	211
	CF	166.8	d	24
	CF_2	99.9	d,d,d	207,14,4
	CF_2	115.1	d	207
	CF	182.6	d,d	14,4
	CF_2	102.8	d,d,d	211,18,6
	CF_2	107.8	d	211
	CF	185.5	d,d	18,6

A mechanism to explain the formation of aromatic products from 1 might begin with expulsion of $CH_2=CF_2$ and HF from 1 to form benzvalene, 8. The two possible aromatization pathways predict the two observed aromatic products.



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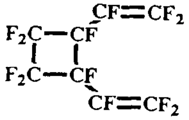
Perfluorobutadiene Dimers

Table 3 gives the nmr parameters of the perfluorobutadiene dimers we identified. As with the cross-dimers, only one isomer of perfluorodivinylcyclobutane 9 was present. It could be eithe the *cis* or *trans*. Perfluorocyclooctadiene 10 and the perfluorinated criss-cross dimer, 11, were easy to identify by their characteristic nmr spectra [1]. There were no peaks assignable to 2+4-adducts or analogs of 5 - 7.



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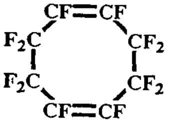

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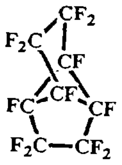

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TABLE 3

Fluorine NMR Data for C_4F_6 Dimers

Compound	Assignment	Chemical Shift	Assignment	Chemical Shift
9	$=CF_2$	87.4	CF	167.7
	$=CF_2$	105.3	CF_2	123.3
	=CF	188.4	CF_2	125.8
10	=CF	128.0	CF_2	119.7
11	=CF	216.2	CF_2	125.5

General Remarks

^{19}F NMR spectra were recorded on a Nicolet NT-220 spectrometer at 188.2 MHz. Chemical shifts are in ppm from $CFCl_3$, upfield = positive.

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