

## Reaction of Organic Compounds with a System SF<sub>4</sub>-HF-Halogenating Agent: XV.\* Reactions of Aliphatic Nitriles with SF<sub>4</sub>-HF-Cl<sub>2</sub>(S<sub>2</sub>Cl<sub>2</sub>)

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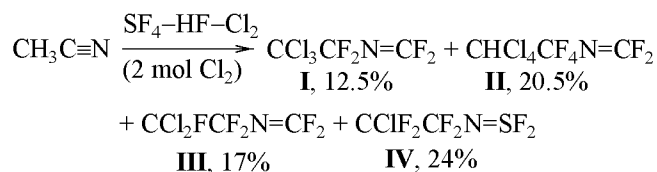
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**Abstract**—Reactions of aliphatic carboxylic acids nitriles with systems SF<sub>4</sub>-HF-Cl<sub>2</sub>(S<sub>2</sub>Cl<sub>2</sub>) were investigated. It was established that the reactions gave rise to iminosulfodifluorides. Therewith besides SF<sub>4</sub> addition across the triple bond of the cyano group occurs also replacement of hydrogen by halogen.

Aliphatic carboxylic acids nitriles are known to suffer transformation when treated with such fluorinating agents as SbF<sub>5</sub>, ClF and F<sub>2</sub> into *N*-chloro-*N*-fluoroamines [2, 3] or into *N,N*-difluoroamines [4, 5], and the reaction of perfluorocarboxylic acids nitriles with chlorine monofluoride affords the corresponding *N,N*-dichloroamines [3, 6, 7]. The reaction of nitriles with sulfur tetrafluoride at 260°C was shown [8] to furnish iminosulfodifluorides.

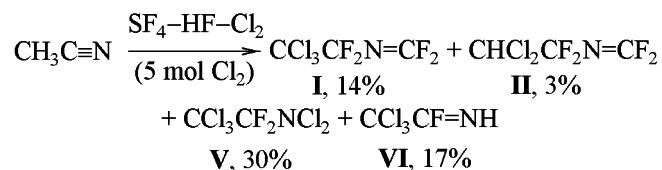
We showed formerly that treatment of unsaturated compounds with SF<sub>4</sub>-HF-Cl<sub>2</sub> resulted in reaction of conjugate chlorofluorination, i.e., the system operates as a stoichiometric equivalent of the chlorine monofluoride [9]. If into the reaction with unsaturated compounds in anhydrous hydrogen fluoride in the presence of S<sub>2</sub>Cl<sub>2</sub> is introduced sulfur tetrafluoride the stoichiometric equivalent of sulfur chloride fluoride S<sub>2</sub>Cl<sub>2</sub> adds across the double bond of the unsaturated compound [10–13]. The process occurs even in the presence of catalytic amounts of sulfur chlorides for the chloride anion arising in the reaction mixture provides additional amount of sulfur chlorides due to reaction with SF<sub>4</sub> [14].

We report here on the study of acetonitrile reaction with a system SF<sub>4</sub>-HF-Cl<sub>2</sub>. It was established that the



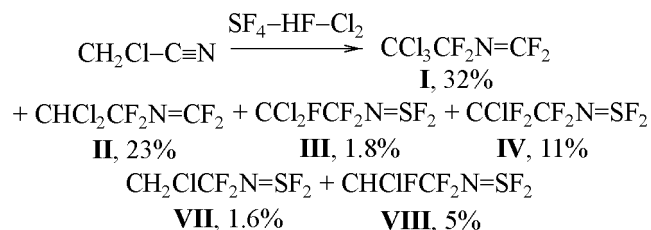
direction of the reaction essentially depends on the amount of chlorine used. The reaction of acetonitrile with the system SF<sub>4</sub>-HF in the presence of a double excess of chlorine formed chlorofluoro-containing iminosulfodifluorides **I–IV**.

At five-fold excess of chlorine and a long reaction time all hydrogens of the methyl group are replaced by chlorine. Therewith the main product is not an iminosulfodifluoride but *N,N*-dichloro-2,2,-trichlorodifluoroethylamine (**V**) and 2,2,2-trichlorofluoroethylimine **VI**.



Evidently in the reaction of acetonitrile with the system SF<sub>4</sub>-HF in the presence of chlorine in a large excess to the cyano group adds prevalingly the chlorine monofluoride and not the sulfur tetrafluoride.

The reaction of monochloroacetonitrile with the system SF<sub>4</sub>-HF-Cl<sub>2</sub> affords a mixture of iminosulfodifluorides **I–IV**, **VII**, **VIII**. Note that the reaction time and temperature do not significantly affect the reaction products ratio.

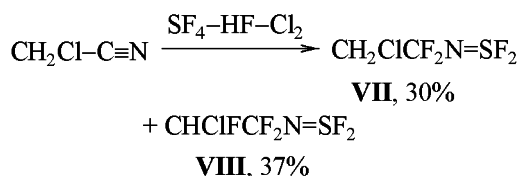


\* For communication XIV see [1].

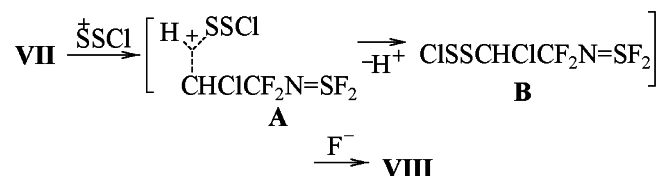
**Table 1.** Reactions of aliphatic carboxylic acids nitriles with the systems SF<sub>4</sub>-HF-Cl<sub>2</sub>(S<sub>2</sub>Cl<sub>2</sub>)

Initial compound	Reagents, g				Reaction conditions		Yield, g	Components content in reaction products	
	initial nitrile	SF <sub>4</sub>	HF	Cl <sub>2</sub> (S <sub>2</sub> Cl <sub>2</sub> )	time, h	temperature, °C		compd. no.	%
CH <sub>3</sub> CN	15.0	60.0	30.0	52.0	20	130	51.0	<b>I</b>	12.5
								<b>II</b>	20.5
CH <sub>2</sub> ClCN	3.0	15.0	10.0	130.0	20	130	13.2	<b>III</b>	17.0
								<b>IV</b>	24.0
								<b>I</b>	14.0
								<b>II</b>	3.0
								<b>V</b>	30.0
								<b>VI</b>	17.0
CHCl <sub>2</sub> CN	3.0	10.0	5.0	8.5	3	130	3.3	<b>I</b>	32.0
								<b>II</b>	23.0
								<b>III</b>	1.8
								<b>IV</b>	11.0
CHCl <sub>2</sub> CN	3.8	6.0	5.0	(2.4)	6	130	3.0	<b>VII</b>	1.6
								<b>VIII</b>	5.0
								<b>VII</b>	30.0
CHCl <sub>2</sub> CN	3.8	6.0	5.0	(2.4)	17	130	3.2	<b>VIII</b>	37.0
								<b>VII</b>	5.0
								<b>VIII</b>	95.0
CHCl <sub>2</sub> CN	3.0	6.0	5.0	0.8	8	130	3.3	<b>I</b>	63.0
								<b>II</b>	27.0
CCl <sub>3</sub> CN	3.0	6.0	5.0	(3.9)	5	130	5.1	<b>II</b>	63.0
								<b>I</b>	96.0
CF <sub>3</sub> (CF <sub>2</sub> ) <sub>5</sub> CN	3.0	8.0	5.0	1.5	5	140	3.5	<b>IX</b>	Quantitative
CF <sub>3</sub> (CF <sub>2</sub> ) <sub>7</sub> CN	3.3	8.0	5.0	1.4	5	150	3.6	<b>X</b>	Quantitative
NC(CF <sub>2</sub> ) <sub>4</sub> CN	4.6	20.0	10.0	6.5	8	170	5.1	<b>XI</b>	90.0

However in reaction of monochloroacetonitrile with the system SF<sub>4</sub>-HF-S<sub>2</sub>Cl<sub>2</sub> only two iminosulfodifluorides **VII**, **VIII** were obtained.



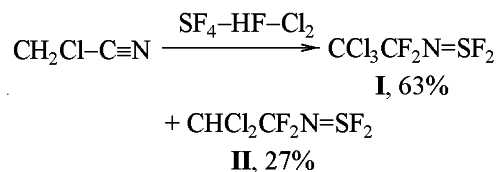
By increasing the reaction time it was possible to obtain predominantly iminosulfodifluoride **VIII**. Apparently compound **VII** under the action of the system SF<sub>4</sub>-HF-S<sub>2</sub>Cl<sub>2</sub> is converted into compound **VIII** along the following scheme:



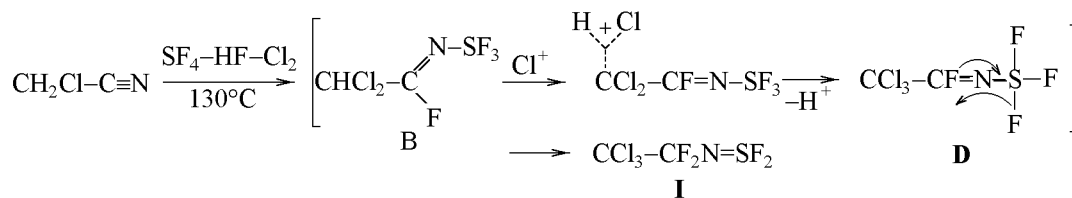
In the first stage one of the hydrogens of the chloromethyl group suffers an attack of cation <sup>+</sup>SSCl

providing a pentacoordinate carbonium ion (A) that eliminates a proton to give the corresponding thiosulfenechloride (B). The replacement in the latter of the thiosulfenechloride group by fluorine results in iminosulfodifluoride **VIII**.

Similarly reacts dichloroacetonitrile with the system SF<sub>4</sub>-HF-Cl<sub>2</sub> providing two iminosulfodifluorides **I** and **II**.

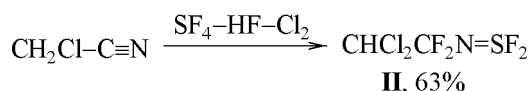


The reaction time does not affect the ratio of compounds **I** and **II** in the product. Besides we demonstrated by a special experiment that the iminosulfodifluoride **II** was not converted into compound **I** when treated with the system 4FSF<sub>4</sub>-HF-Cl<sub>2</sub>. Apparently the methyl group is chlorinated in fluorosulfurane (C) formed at the earlier reaction stage or



reaction analogous to halogenation of acyl chlorides by reaction of Hell-Volhard-Zelinsky.

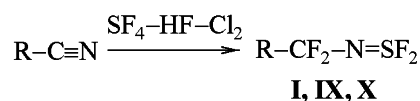
In reaction of dichloroacetonitrile with the system  $\text{SF}_4\text{-HF-S}_2\text{Cl}_2$  formed only iminosulfodifluoride **II**.



Presumably the presence of two chlorine atoms in the dichloromethyl group prevents by steric hindrance the formation of pentacoordinate carbonium ion at the attack of the  $^+\text{SSCl}$  cation, and the reaction of

dichloroacetonitrile in the system  $\text{SF}_4\text{-HF-S}_2\text{Cl}_2$  occurs only at the triple bond of the cyano group.

The reaction of trichloroacetonitrile and perfluorocarboxylic acids nitriles with the system  $\text{SF}_4\text{-HF-S}_2\text{Cl}_2$  at 140–170°C afforded in nearly quantitative yield the products of  $\text{SF}_4$  addition across the  $\text{C}\equiv\text{N}$  bond of the nitriles:



$\text{R} = \text{CCl}_3$  (**I**),  $\text{C}_6\text{F}_{13}$  (**IX**),  $\text{C}_8\text{F}_{17}$  (**X**).

**Table 2.** Characteristics of  $^1\text{H}$  and  $^{19}\text{F}$  NMR spectra of compounds obtained

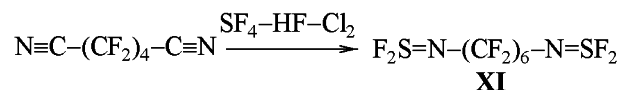
Compd. no.	Formula	Chemical shifts, $\delta$ , ppm		<i>J</i> , Hz
		$^1\text{H}$	$^{19}\text{F}$	
<b>I</b>	$\text{CCl}_3\text{CF}_2\text{NSF}_2^2$	–	79.02 t ( $2\text{F}^1$ ) –54.72 t ( $2\text{F}^2$ )	19 ( $\text{F}^1 - \text{F}^2$ )
<b>II</b>	$\text{CHCl}_2\text{CF}_2\text{NSF}_2^2$	5.69 t	80.69 t ( $2\text{F}^1$ ) –56.17 t ( $2\text{F}^2$ )	5 ( $\text{H} - \text{F}^1$ ) 19 ( $\text{F}^1 - \text{F}^2$ )
<b>III</b>	$\text{CCl}_2\text{F}^1\text{CF}_2\text{NSF}_2^3$	–	81.17 t.t ( $1\text{F}^1$ ) 75.45 m ( $2\text{F}^2$ ) –54.57 m ( $2\text{F}^3$ )	9 ( $\text{F}^1 - \text{F}^2$ ) 4 ( $\text{F}^1 - \text{F}^3$ ) 19 ( $\text{F}^2 - \text{F}^3$ )
<b>IV</b>	$\text{CClF}_2^1\text{CF}_2\text{NSF}_2^3$	–	82.57 q ( $2\text{F}^1$ ) 84.17 t.t ( $2\text{F}^2$ ) –52.8 t.t ( $2\text{F}^3$ )	4 ( $\text{F}^1 - \text{F}^2$ ) 4 ( $\text{F}^1 - \text{F}^3$ ) 17 ( $\text{F}^2 - \text{F}^3$ )
<b>V</b>	$\text{CCl}_3\text{CF}_2\text{NCl}_2$	–	87.91 s	–
<b>VI</b>	$\text{CCl}_3\text{CF}=\text{NH}$	5.1 m	91.05 d	18 ( $\text{H} - \text{F}$ )
<b>VII</b>	$\text{CH}_2\text{ClCF}_2\text{NSF}_2^2$	3.90 t	85.57 m ( $2\text{F}^1$ ) –56.7 t ( $2\text{F}^2$ )	10 ( $\text{H} - \text{F}^1$ ) 17 ( $\text{F}^1 - \text{F}^2$ )
<b>VIII</b>	$\text{CHClF}^1\text{CF}_2\text{NSF}_2^3$	6.42 d.m	89.87 d.m ( $1\text{F}^1$ ) 85.31 m ( $2\text{F}^2$ ) –55.3 m ( $2\text{F}^3$ )	48 ( $\text{H} - \text{F}^1$ ) 3 ( $\text{F}^1 - \text{F}^3$ )
<b>IX</b>	$\text{CF}_3^6\text{CF}_2^5\text{CF}_2^4\text{CF}_2^3\text{CF}_2^2\text{CF}_2^1\text{CF}_2^7\text{NSF}_2^8$	–	33.78 m ( $4\text{F}^{1,2}$ ) 32.89 m ( $2\text{F}^3$ ) 30.93 m ( $2\text{F}^4$ ) 29.15 t.m ( $2\text{F}^5$ ) 73.99 t ( $3\text{F}^6$ ) 74.57 t ( $2\text{F}^7$ ) –53.64 t ( $2\text{F}^8$ )	9 ( $\text{F}^5 - \text{F}^6$ ) 20 ( $\text{F}^7 - \text{F}^8$ )
<b>X</b>	$\text{CF}_3(\text{CF}_2)_7\text{CF}_2\text{NSF}_2^2$	–	74.35 t.t ( $2\text{F}^1$ ) –57.15 t ( $2\text{F}^2$ )	21 ( $\text{F}^1 - \text{F}^2$ )
<b>XI</b>	$\text{CF}_2^1\text{CF}_2^2\text{CF}_2^3\text{N}=\text{CF}_2^4$ $\text{CF}_2^1\text{CF}_2^2\text{CF}_2^3\text{N}=\text{CF}_2^4$	–	31.25 m ( $2\text{F}^1$ ) 34.06 m ( $4\text{F}^2$ ) 74.9 t.m ( $4\text{F}^3$ ) –53.95 t ( $4\text{F}^4$ )	20 ( $\text{F}^3 - \text{F}^4$ )

**Table 3.** Physical constants and elemental analyses of compounds obtained

Compd. no.	bp, °C (p, m Hg)	n <sub>D</sub> <sup>20</sup>	Found, %		Formula	Calculated, %	
			F	S		F	S
<b>I</b>	130–131	1.4197	29.9, 29.6	12.5, 12.7	C <sub>2</sub> Cl <sub>3</sub> F <sub>4</sub> NS	30.1	12.67
<b>II</b>	110–112	1.4285	34.9, 34.3	15.2, 14.9	C <sub>2</sub> HCl <sub>2</sub> F <sub>4</sub> NS	34.86	14.68
<b>IV</b>	63–64	–	52.1, 52.5	15.1, 14.7	C <sub>2</sub> ClF <sub>6</sub> NS	51.94	14.58
<b>V</b>	78–81 (3)	–	14.1, 14.8	71.0, 70.4 <sup>a</sup>	C <sub>2</sub> Cl <sub>5</sub> F <sub>2</sub> N	14.59	70.02 <sup>a</sup>
<b>VI</b>	61–65 (30)	–	11.8, 11.3	65.1, 65.8 <sup>a</sup>	C <sub>2</sub> HCl <sub>3</sub> FN	11.55	64.74 <sup>a</sup>
<b>VII</b>	105–107	1.4365	41.08, 41.32	17.11, 17.09	C <sub>2</sub> H <sub>2</sub> ClF <sub>4</sub> NS	41.42	17.44
<b>VIII</b>	85–87	–	46.8, 47.5	16.1, 16.4	C <sub>2</sub> HClF <sub>5</sub> NS	47.15	15.89
<b>IX</b>	133–134	1.3035	70.8, 70.1	7.3, 7.1	C <sub>7</sub> F <sub>17</sub> NS	71.3	7.09
<b>X</b>	167–168	1.3070	72.8, 72.2	5.1, 5.6	C <sub>9</sub> F <sub>21</sub> NS	72.15	5.79
<b>XI</b>	183–184	1.3382	65.1, 64.4	14.2, 13.4	C <sub>6</sub> F <sub>16</sub> N <sub>2</sub> S <sub>2</sub>	64.96	13.68

<sup>a</sup> Fluorine content is given.

Similarly occurs the reaction between the system SF<sub>4</sub>-HF-Cl<sub>2</sub> and 1,4-dicyanoperfluorobutane



The formation in these reactions of compounds containing an N=SF<sub>2</sub> group is confirmed by <sup>19</sup>F NMR spectra: in the spectra of all iminosulfodifluorides appears a signal in the region -52÷-57 ppm characteristic of fluorine atoms attached to sulfur.

It should be noted that these reactions occur at 140–170°C affording the products in almost quantitative yield whereas with SF<sub>4</sub> only the required temperature is 220–250°C and the yield of iminosulfodifluorides does not exceed 30% [8].

Thus in reactions of the systems SF<sub>4</sub>-HF-Cl<sub>2</sub>(S<sub>2</sub>Cl<sub>2</sub>) with hydrogen-containing nitriles occurs not only addition of SF<sub>4</sub> to the cyano group followed by isomerization but also replacement of hydrogens in the methyl group by chlorine or fluorine.

#### EXPERIMENTAL

<sup>1</sup>H and <sup>19</sup>F NMR spectra were registered on spectrometer Tesla BS-497 at operating frequencies 100 and 94.075 MHz respectively from 50% solutions in (CD<sub>3</sub>)<sub>2</sub>CO. Chemical shifts were measured respectively from HMDS as internal reference and CCl<sub>3</sub>F as external reference. GLC analysis was carried out on chromatograph LKhM-80 equipped with a steel columns 1000×3 mm with the stationary phase 5% SE-30 on Cromosorb W(AW-DMCS) and 3000×3 mm with the stationary phase 15% PEG-20000 on the same solid carrier; detector katharometer, carrier gas helium.

Nitriles of perfluoropelargonic, perfluoroanthic acid and dicyanoperfluorobutane were obtained as described in [15] from the corresponding carboxylic acids and adipic acid. Acetonitrile was dried on P<sub>205</sub> and distilled. The sulfur tetrafluoride was prepared by Tullock procedure [16].

Reaction of nitriles with the systems SF<sub>4</sub>-HF-Cl<sub>2</sub>(S<sub>2</sub>Cl<sub>2</sub>) (general procedure). A mixture of initial reagents was heated in stainless steel pressure reactors of 50 or 250 ml capacity. The gases of reaction were removed by passing through a saturated alkali solution, the content of the reactor was poured on ice, washed with water. The organic layer was separated and dried on Na<sub>2</sub>SO<sub>4</sub>. The reaction products were isolated by distillation or preparative GLC.

The conditions of reactions between nitriles and the systems SF<sub>4</sub>-HF-Cl<sub>2</sub>(S<sub>2</sub>Cl<sub>2</sub>) are listed in Table 1. Physical constants, elemental analyses of compounds obtained and the characteristics of their <sup>1</sup>H and <sup>19</sup>F NMR spectra are given in Tables 3 and 2 respectively.

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