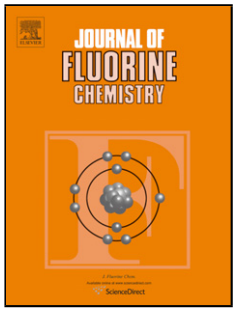

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Novel synthetic route to perfluoroallyl cyanide (PFACN) reacting perfluoroallyl fluorosulfonate with cyanide

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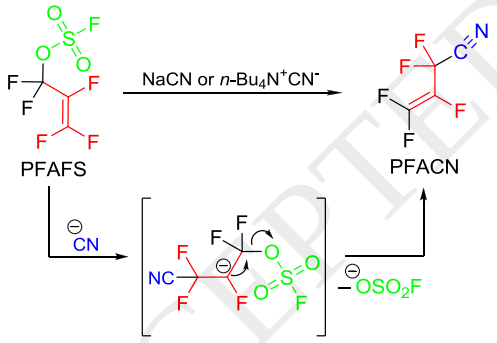

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Highlights:

- a novel synthetic method for the preparation of PFACN
- by ^{19}F-,^{13}C-NMR and IR spectroscopy characterized
- by MS-spectrometry characterized
- up to 30% isolated yield
- optimized reaction conditions

Abstract: A novel synthetic method for the preparation of perfluoroallyl cyanide CF_2=$CFCF_2CN$ (PFACN) is presented. This includes the addition – elimination reaction of cyanide anion with perfluoroallyl fluorosulfate CF_2=$CFCF_2OSO_2F$ (PFAFS). The reaction conditions, factors affecting the reactivity and regioselectivity of the process, the choice of reagent as well as the course of competitive reactions are discussed, too.

Keywords: perfluoroallyl fluorosulfate, perfluoroallyl cyanide, addition/elimination reactions, cyanide anion.

1. Introduction

In recent years, unsaturated perfluorinated nitriles have found important application in the synthesis of selected amorphous fluoroplastics such as crosslinkers (Fig. 1). However, among the co-polymers of this class described in literature, nitriles containing the perfluorovinyl moiety are of great interest (**A** and **B**) [1-3]. The classical unsaturated perfluorinated nitriles are represented by only one example, namely perfluoroallyl cyanide (**C**, Fig. 1). This compound can be used successfully for the synthesis of amorphous tetrafluoroethylene-hexafluoropropylene copolymer as well as in the preparation of films, coatings, additives, encapsulants, and mold release agents [4-7]. PFACN also finds application for plasma etching silicon-containing films to produce electronic components or semiconductor devices [8-9].

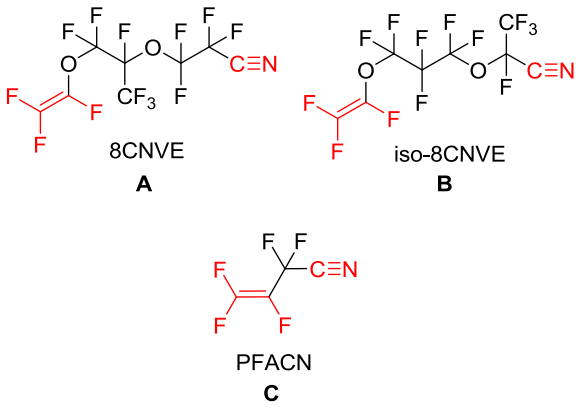


Fig. 1. Some examples of unsaturated perfluorinated nitriles as copolymers for amorphous fluoroplastics

However, very few examples of synthetic routes to PFACN have been described and only two reports could be found in the literature as shown in Fig. 2 [10-11]. In the first example, PFACN was obtained by dechlorination of 3,4-dichloropentafluoro butyronitrile with zinc in dioxane [10]. In the second example, PFACN was synthesized upon treatment of 3-chloro-1,1,2,3,3-pentafluoroprop-1-ene with sodium cyanide (NaCN) in aqueous *tert*-butanol [11]. However, in both cases the literature sources have not provided any information about the isolated yield of the products as well as the spectral characteristics of PFACN. Moreover, the description of the synthetic procedure has either not been presented [10] or published with limited information [11]. In addition, the determined boiling points of PFACN differ significantly, namely 26 °C for ref. [10] and 43 – 48 °C for ref. [11], respectively. Certain doubts about the reliability of the results have been also caused by using water as the reaction medium in the synthesis of PFACN [11]. Therefore, the important role of PFACN in industrial polymerization processes [1-7], the inaccessibility of its known precursors [10-11], as well as the inconsistency of the described methods [10-11], renders the search for a convenient method of obtaining PFACN an actual research objective.

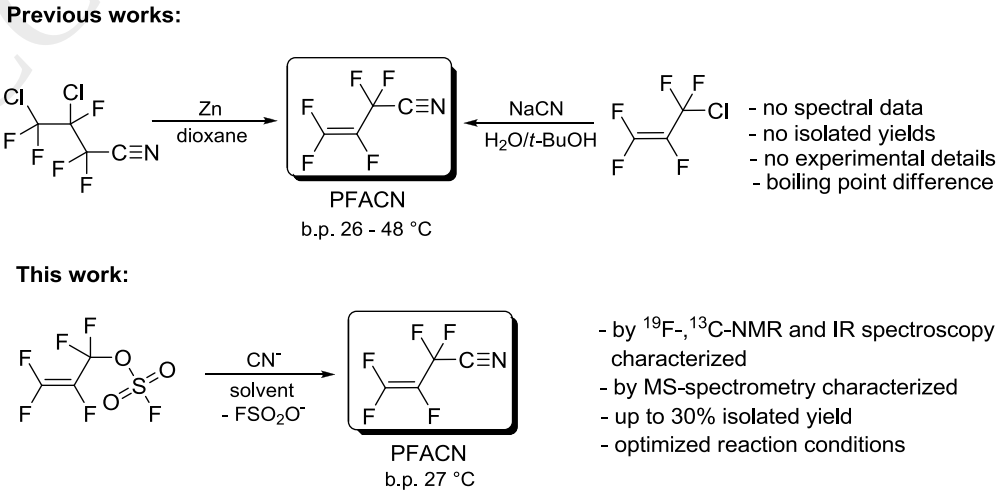


Fig. 2. Previous works and current work

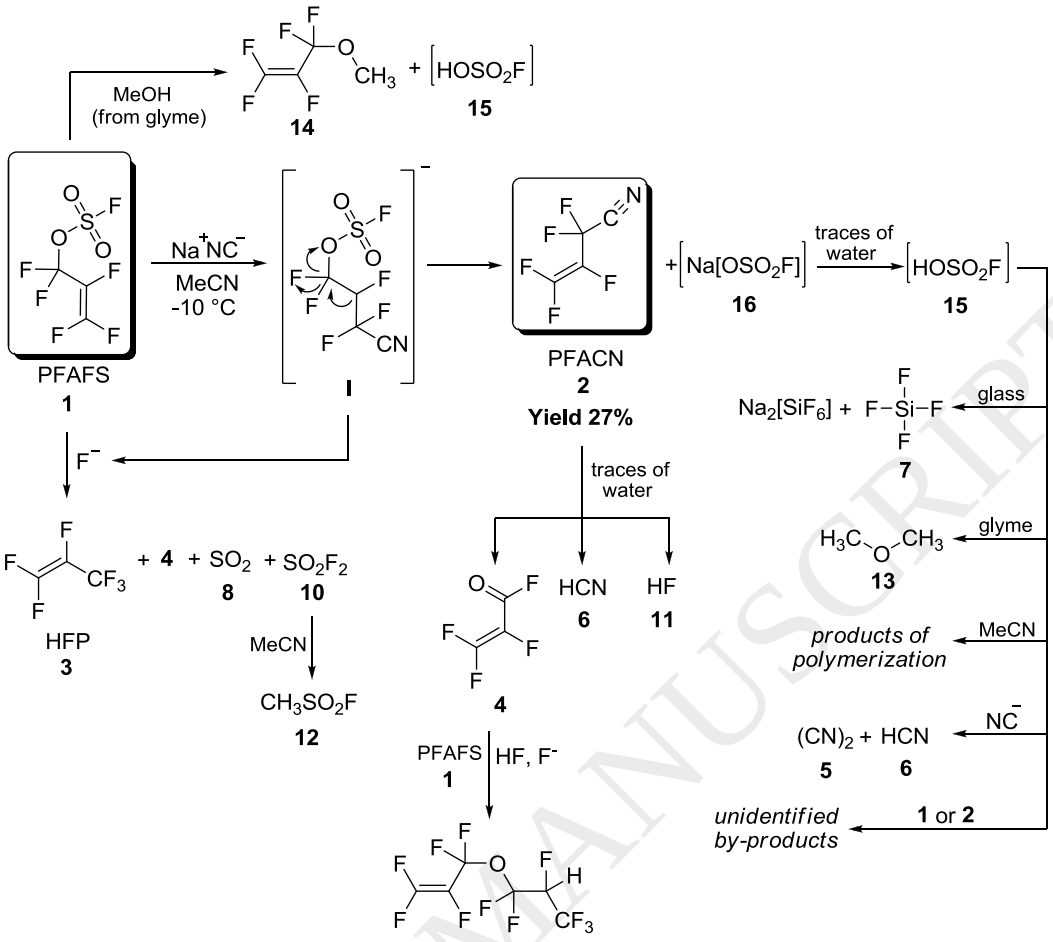
It is well known that perfluoroallyl fluorosulfate (PFAFS) is a convenient building block for the preparation of various fluoroallyl compounds [12-13]. The fluorosulfate group is a good leaving group and could be easily replaced by a variety of nucleophilic reagents. This process is usually conducted through addition of a nucleophile to the double bond of PFAFS, prior to the elimination of the fluorosulfate anion (Scheme 1). As nucleophiles, various alcohols, phenols, perfluoroalcoholates, azides and halides could be applied [12]. Furthermore, no examples for reacting PFAFS with cyanide anion sources have been described, so far. For the first time a convenient production of PFACN *via* the reaction of PFAFS with cyanide is reported.

2. Results and discussion

2.1. Preparation

Perfluoroallyl fluorosulfate (PFAFS) actively reacts with sodium cyanide to form perfluoroallyl cyanide (PFACN) as the main product. The reaction was carried out by slow addition of PFAFS **1** to a suspension of NaCN in an organic solvent (Scheme 1) to furnish PFACN **2** in 24 – 27 % yields (Method A). The reaction was highly exothermic possessing a cumulative effect. If the temperature of the reaction mixture was raised above -10 °C, an uncontrollable process was initiated that spontaneously increased the temperature of the reaction mixture up to 75 – 80 °C. Moreover, destruction and polymerization of **1** occured, and product **2** was not detected even in traces. The optimal temperature should be around -16 ÷ -10 °C (Table 1, entries 1 and 2) and the selectivity of the reaction of NaCN with PFAFS **1** strongly depends on the solvent. Hence, a wide range of different solvents, such as water, acetone, acetonitrile (CH_3CN), methanol (CH_3OH), diglyme (DG), triglyme (TG), dichloromethane (DCM), Hostinert-216, *N*-methyl-2-pyrrolidone (NMP), as well as a mixture of solvents (CH_3CN/H_2O) were tested. The best results were obtained using aprotic solvents of medium polarity including CH_3CN or TG. As a result, compound **2** was obtained in 27% and 18% yield, respectively (entries 1 and 3). In the case of highly polar NMP, the reaction proceeded non-regioselectively and according to GC-MS and ^{19}F NMR PFACN **2** was not formed (entry 4). In the case of non-polar Hostinert-216, the reaction did not lead to completion and the sprecursor **1** could be quantitatively recovered (entry 5). The presence of water in the reaction mixture, even in catalytic amounts (entry 6), led to a sharp decrease in the selectivity of the process and **2** could be only registered in traces by GC-MS (entry 7). An excess of NaCN and the choice of solvent affected the efficiency of the reaction: in the case of acetonitrile, an increase in the amount of NaCN from 1.1 to 1.98 equiv. led to higher yields of **2** - from 13% to 27% (entries 8 and 1).

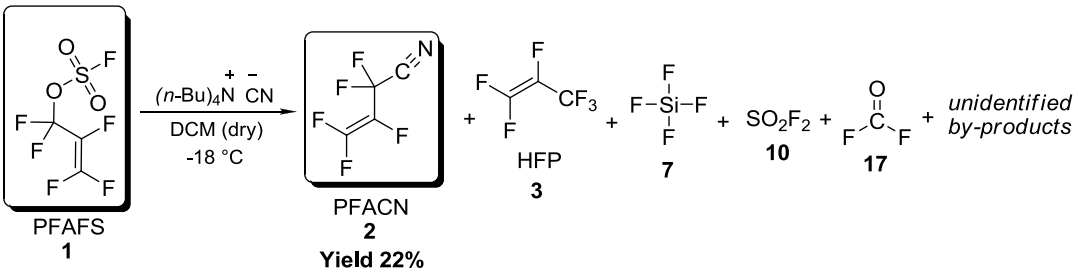
Regarding TG as a solvent, there is an opposite trend and an increase in the amount of reagent from 1.0 to 1.95 equiv. led to a loss of yield of **2** from 18% to 11% (entries 3 and 9). Aiming to improve the thermal control of the reaction, the order of addition of reagents was changed and pre-dried NaCN was added to the solution of PFAFS **1** in anhydrous MeCN at -10 ° C under intense stirring. However, after addition of the first portion of NaCN, no visual effects of the process were observed. To avoid an uncontrollable exothermic reaction, further 0.2 equiv. of NaCN were added to the reaction mixture which was slowly warmed to ambient temperature until the reaction started. Nevertheless, the reaction proceeded very slowly, accompanied by darkening of the mixture and the formation of resinous by-products. After addition of 1.3 equiv. of NaCN in portions, the conversion of **1** reached only 25%, and the yield of **2** was only 4% (entry 10). The reaction course was additionally controlled by GC-MS spectrometry and ^{19}F NMR spectroscopy. In this case, except for the starting material **1** and product **2**, the following by-products were identified in the reaction mixture: hexafluoropropene (HFP) **3**, CF_2=CF-C(O)F **4**, dicyane **5**, HCN **6**, SiF_4 **7**, SO_2 **8**, CF_2=CF-CF_2-O-CF_2-CFH-CF_3 **9**, SO_2F_2 **10**, HF **11** and CH_3SO_2F **12**. Using diglyme (DG) or TG as a solvent, also CH_3-O-CH_3 **13** and CF_2=CF-CF_2-OCH_3 **14** were detected in the reaction mixture. Based on these results possible reaction routes of **1** with NaCN in MeCN or glymes might be suggested (Scheme 1). Obviously, the main factor that influenced the regioselectivity of the reaction was the elimination of the fluoride anion, which competed with the elimination of fluorosulfonate anion leading to the stabilization of the intermediate **I** (Scheme 1). According to the hard soft acid base Lewis [14] and Pearson [15] theories, the fluoride anion is considered as a "hard base" [16], and its nucleophilicity strongly depends on its solvation (nature of solvent) and the degree of abstraction (nature of a cation). The fluoride anion could initiate not only the destruction of the starting material **1**, but also the decomposition of the product **2** leading to the formation of HFP **3**, carbonyl fluoride **4**, SO_2 **8** and SO_2F_2 **10**. Subsequent interaction of **10** with acetonitrile gave probably **12**, which was detected by ^{1}H and ^{19}F NMR spectroscopy (doublet at δ_H 2.2 ppm with $^3J_{HF}$ = 7.1 Hz and quartet at δ_F +50.9 with $^3J_{FH}$ = 7.1 Hz) [17]. Apart from this, the traces of methanol present in DG and TG might interact with PFAFS **1** giving rise to allyl ether **14** and fluorosulfonic acid **15** (Scheme 1).



Scheme 1 General scheme and possible reaction pathways of PFAFS **1** with NaCN

Traces of water in the solvent also influenced the reaction course. We postulated that HF **11**, HCN **6** and carbonyl fluoride **4** were formed in the reaction mixture as a result of hydrolysis of PFACN **2**. Its further condensation with PFAFS **1** and HF **11** furnished the *H*-containing ether **9**. Na[FSO_3] **16** formed during the reaction course could also be protonated producing free fluorosulfonic acid **15**. The reaction of **15** with cyanide anion could be explained experimentally by the presence of cyanogen **5** and plausibly HCN **6** in the reaction mixture (GC-MS). Super acid **15** probably induced the polymerization of acetonitrile and the formation of dimethyl ether **13** in glymes (DG and TG) as solvents (Scheme 1). The presence of FSO_3H **15** or HF **11** in the reaction mixture could be also confirmed by the formation of silcontetrafluoride **7** as a result of the reaction with glass. Moreover, a broad signal at δ_H 12.6 ppm in ^{1}H NMR also proved the presence of acidic components in the reaction mixture. With the aim to neutralize these acids, strong and non-nucleophilic bases such as *N*-ethyldi*iso*propylamine (Hünig's base) or diazabicyclo[5.4.0]-undec-7-en (DBU) were applied in catalytic amounts as well as 30% water ammonia solution as an additive. As seen from the presented results (entries 11–12), the application of DBU and Hünig's base increased the degree of

destruction of **1** leading to the loss of yield of **2** up to 9 – 10 %. Upon addition of NH_3(aq) the reaction mixture became very viscous and PFACN **2** was not detected even in traces (entry 13). These results could be explained by strong tendency of cations $(i\text{-Pr})_2EtNH^+$ and $DBUH^+$ to the abstraction of a fluoride anion in comparison to Na^+, that led to an increase in destruction of **1** and to a decrease in the yield of **2**. The substitution of NaCN through KCN significantly increased the reactivity of the substrate. However, it was not possible to conduct the process thermodynamically controlled. After addition of the larger amount of PFAFS **1** to the suspension of KCN in acetonitrile at -10 ÷ -15 °C, the temperature of the reaction mixture spontaneously raised up to 76 °C and quantitative decomposition of the starting **1** and **2** was observed (entry 14). Another factor that influenced the decomposition of **1** and **2** probably included the higher ability of fluoride abstraction by K^+ in comparison to Na^+. On the other hand, the process *via* addition of PFAFS **1** at 60 – 65 °C with pre-dried KCN was not successful and **1** was recovered in quantitative yield. Moreover, PFACN **2** was not detected even in traces (entry 15). This phenomenon could be best explained by the insolubility of KCN even in boiling PFAFS **1**. Ineffective control of the reaction temperature in combination with a strong "cumulative effect" as a consequence can be associated with very low solubility of NaCN and KCN in MeCN [18]. Therefore, it was of interest to test $n\text{-Bu}_4N^+CN^-$ as a cyanide-anion source which is very well soluble in a variety of organic solvents [19]. High solubility of this reagent, e.g. in acetonitrile (70 g/100 mL, [19]) allowed to carry out the reactions under homogeneous conditions. Furthermore, the direct addition of **1** to a solution of $n\text{-Bu}_4N^+CN^-$, as well as reverse addition of a 70% solution of $n\text{-Bu}_4N^+CN^-$ to the solution of **1** were investigated. The tendency of the tetrabutylammonium cation to abstract F^- is especially great and the solubility factor (solvation effect) should play even a more important role. Upon addition of PFAFS **1** to the solution of tetrabutylammonium cyanide (TBACN) cooled to -20 ÷ -15 °C in MeCN or DG, a strong exothermic reaction was observed accompanied by noticeable production of resinous by-products. Despite a reliable temperature control and the absence of spontaneous "temperature surges", PFACN **2** either was not detected at all (entry 16) or was registered in only traces (entry 17) according to ^{19}F NMR. The conversion of PFAFS **1** was 65 and 50 mol%, respectively. Better results were obtained through addition of the solution of $n\text{-Bu}_4N^+CN^-$ to the acetonitrile solution of **1** in at -20 ÷ -17 °C. Despite low conversion of **1** (49 mol%) and polymerization of MeCN, the content of **2** in the reaction mixture was 13 mol%, and the yield of product 7% (entry 18). However, if the reaction was conducted under similar conditions, but in the less polar solvent dichloromethane (DCM), the conversion of **1** was 100% and the content of **2** in the reaction mixture was 80 mol% according to ^{19}F NMR (Scheme 2).



Scheme 2 Reaction route of PFAFS **1** with *n*-$Bu_4N^+CN^-$ in dichloromethane

Due to the formation of by-products, which were difficult to separate, the isolated yield of PFACN **2** was only 22 % (entry 19, Method B). In this manner, the fluoride anion abstraction using *n*-$Bu_4N^+F^-$ and the decrease of the polarity of the solvent positively influenced both the regioselectivity of the process as well as the increase in yield of the target product **2**. During the experiments with *n*-$Bu_4N^+CN^-$ only pre-dried MeCN, DG, and DCM were used. Thus, the monitoring of the reaction mixture by ^{19}F NMR showed the absence of carbonyl fluoride **3** and allyl ether **7** (in the case of DG). The main by-products (**1**, **5**, **8,** and **9)** were also detected (Scheme 2) as in the course of the reaction with NaCN (Scheme 1). This indicates, the reaction of PFAFS **1** with CN^- is based on general principles and do not depend on the type of the cation.

Table 1

Screening of reaction conditions of PFAFS **1** with various sources of CN^-

Entry	Cyanide	Additive, %	Mol. ratio of PFAFS **1** : CN^-	Solvent	Time, hrs	T, °C	Yield (%)[a]
1	NaCN	-	1 : 1.98	MeCN	2.0	-10	**27**
2	NaCN	-	1 : 1.87	MeCN	18.0	-16 ÷ -10	24
3	NaCN	-	1 : 1.02	TG	2.5	-10 ÷ 60	18
4	NaCN	-	1 : 1.95	NMP	2.0	-10 ÷ 24	-[d]
5	NaCN	-	1 : 1.02	Hostinert-216	3.0	-13	-[d]
6	NaCN	H_2O, 2.4	1 : 1.95	MeCN	2.0	-15	< 1[d]
7	NaCN	-	1 : 1.02	H_2O	2.5	24	< 1[d]
8	NaCN	-	1 : 1.1	MeCN	3.0	-5 ÷ 2	13
9	NaCN	-	1 : 1.95	TG	2.5	-10 ÷ 60	11
10	NaCN[b,c]	-	1 : 1.3	MeCN[b]	10.0	-10 ÷ 24	4
11	NaCN	*i*-Pr_2EtN, 3.0 Hydroquinone, 1.0	1 : 1.8	DG	2.0	-5 ÷ 5	10

12	NaCN	DBU, 5.0	1 : 1.02	MeCN	3.0	-13	9
13	NaCN	30% NH_3(aq), 12	1 : 1.98	MeCN	2.0	-18 ÷ -14	-[d]
14	KCN	-	1 : 1.02	MeCN	2.0	-15 ÷ 76	-[d]
15	KCN[b]	-	1 : 4.0	-	1.5	60 ÷ 65	-[d]
16	TBACN	-	1 : 1.05	MeCN[b]	2.5	-20 ÷ -15	-[d]
17	TBACN	-	1 : 1.01	DG[b]	2.0	-15	< 1[d]
18	TBACN[c]	-	1 : 1.1	MeCN[b]	3.0	-20 ÷ -17	7
19	TBACN[c]	-	1 : 1.1	DCM[b]	4.0	-20 ÷ -17	**22**

a) Isolated yield

b) Dried under normal conditions

c) The cyanide was added to the solution of **1** in organic solvent (*Method B*).

d) According to ^{19}F NMR analysis of the reaction mixture.

2.2. Characterization

Perfluoroallyl cyanide **2** is a colorless liquid with a b.p. 27 °C/760 mmHg. PFACN **2** could be stored under inert atmosphere at 0 °C for months, without any changes. The purity of **2** was *ca.* 92% according to GC-MS spectrometry and ^{19}F NMR spectroscopy. The structure of **2** was unequivocally elucidated using all spectroscopic methods. like ^{19}F, ^{13}C NMR, IR spectroscopy and MS-spectrometry. In the ^{19}F NMR spectrum, a typical splitting pattern for perfluorinated compounds is observed including three magnetically non-equivalent fluorine nuclei: CF_2(A,B)=CF(C) at δ_F ~ -89 (A), -104 (B) and -192 (C) ppm with $^{gem}J_{FF}$ = ~ 50 Hz, $^{cis}J_{FF}$ = ~ 39 Hz and $^{trans}J_{FF}$ = ~ 117 Hz. A signal corresponding to allylic fluorine nuclei from CF_2-group is observed at about δ_F ~ -94 ppm as a doublet of doublet of doublets (ddd) with $^{allyl}J_{FF}$ = ~ 20 Hz. Signals of CF_2-group were markedly downfield shifted in comparison with PFAFS **1** (δ_F ~ -73 ppm [12]). By ^{19}F NMR spectroscopy, the disappearance of the SO_2F signal (δ_F ~ +46 ppm [12]) can unambiguously distinguish between PFACN **2** and **1** in a mixture. In the ^{13}C NMR spectrum of **2**, a typical set of signals of an allylic fragment at δ_C ~ -156 ppm (CF_2=), -123 ppm (=CF-) and -105 ppm (-CF_2) with $^1J_{CF}$ = ~ 240 – 290 Hz and $^2J_{CF}$ = ~ 30 – 40 Hz could be detected. The carbon nucleus from the nitrile group is registered at approximately δ_C ~ -110 ppm with $^2J_{CF}$ = 45 Hz. In the IR-spectrum of PFACN strong bands at ν = 2261, 1792, 1371, 1164, 1123 and 974 cm^{-1} could be distinguished which are typical for vibrational absorptions of C≡N, C=C, C–C–C, C–C–CN, F–C–F and C–F, respectively. Multiple bands in the region 2800 – 3000 cm^{-1} probably indicated the presence of CH_3CN traces in the product. Mass spectrometry refers to the most convenient and unambiguous methods for verification of the target product **2**. An intensive $M^{+\bullet}$-peak with *m/z* 157

proved the formation of PFACN **2**. Signals with *m/z* 138 [M-F] and 131 [M-CN] showed that the main fragmentation route of $M^{+\bullet}$ is the elimination of F or CN fragment. The presence of other fragmentation products with *m/z* 107 [M-CF_2], 81 [C_2F_3], 76 [CF_2CN] and 50 [CF_2] also confirm the proposed fragmentation pathway of **2**.

3. Conclusions

For the first time we reported a simple and convenient method for the synthesis of perfluoroallyl cyanide (PFACN) **2** *via* addition reaction of the cyanide anion to the double bond of perfluoroallyl fluorosulfate **1**, followed by the elimination of the fluorosulfate anion as a leaving group. Various cyanide sources (NaCN, KCN, *n*-$Bu_4N^+CN^-$), solvents (MeCN, DG, TG, water, NMP, Hostinert-216, DCM) and reaction conditions were tested. The best results were obtained by the addition of PFAFS to a suspension of sodium cyanide in acetonitrile or by the addition of a solution of *n*-$Bu_4N^+CN^-$ in anhydrous DCM to PFAFS. As a result, the desired PFACN **2** was furnished in 27% or 22% yields, respectively. The main reaction routes and factors affecting the activity and regioselectivity of the process as well as the formation of by-products were presented. The structure of perfluoroallyl cyanide **2** was fully established and the product **2** was for the first time characterized by NMR, IR spectroscopy and MS spectrometry.

4. Experimental

4.1. General

All reactions were carried out in glass reaction vials under an atmosphere of dry Ar. Before use, MeCN and DCM were freshly distilled from CaH_2. DG was distilled from sodium / benzophenone and used immediately. Unless otherwise noted, all reagents and starting materials were purchased from commercial sources and used without further purification. PFAFS was synthesized following a common procedure [12] with the purity of 93% (GC-MS). *n*-$Bu_4N^+CN^-$ was synthesized according to the reported procedure [19]. All boiling points are uncorrected. ^{13}C NMR spectra were recorded at 100 MHz, ^{19}F NMR spectra were recorded at 376 MHz on JEOL ECX 400 MHz spectrometer. ^{13}C and ^{19}F NMR chemical shifts (δ) are reported in ppm from tetramethylsilane and $CFCl_3$, using the residual solvent resonance (CD_3CN: δ_C 118.1 and 1.2 ppm) as an internal reference. Coupling constants (*J*) are given in Hz. IR spectra were measured on Nicolet Magna 560 spectrometer at atmospheric pressure. GC–MS was conducted on Agilent 6890A.

*4.2. Synthesis of PFACN **2***

4.2.1. Method A

A 500-mL three-necked round-bottom flask, equipped with a magnetic stirrbar, reflux condenser, a dropping funnel, thermometer, and a bubble counter was charged with NaCN (42.5 g, 0.87 mol) suspended in MeCN (211 g, 245 mL) in the atmosphere of dry nitrogen. The suspension was cooled to -10 °C and PFAFS **1** (100.3 g, 0.44 mol) was slowly added within 2.5 hours. At the same time, a strong exothermic was observed and the temperature raised up to 4.4 °C. In this case the addition of **1** immediately ceased and the temperature of the reaction mixture decreased again to -10 °C. After addition of **1,** the reaction mixture was stirred for 2 hours at -10 °C and afterwards it was distilled under reduced pressure. The following fractions were collected: fraction 1 (19.9 g, < 15 °C / 300 mmHg), fraction 2 (22.9 g, 30 °C / 300 mmHg), fraction 3 (2.5 g, > 50 °C / 293 mmHg). Then, the fraction 1 was additionally distilled with a short Vigreux column. The fraction with b.p. 26 – 27 °C/760 mmHg was collected. **2** was obtained in 27% yield (18.6 g) as a colorless liquid.

4.2.2. Method B

In a 100-mL three neck flask equipped with thermometer, dropping funnel and distillation set connected to a trap cooled to -80 °C (10.5 g, 6.2 mL, 45.6 mmol) PFAFS **1** and dry DCM (24 mL) were placed. The reaction mixture was cooled to -20 °C and the solution of TBACN (13.6 g, 50.7 mmol) in dry DCM (35 mL) was slowly added dropwise upon intense stirring (the temperature should not exceed -17 °C). An exothermic effect was observed and the reaction mixture turned dark. Subsequently, the cooling bath was removed. The reaction mixture was warmed to r.t. and was mixed at this temperature for 4 hours. Afterwards, the reaction mixture was distilled using a distillation set with a short Vigreux column. The fraction with b.p. 27 – 28 °C/760 mmHg was collected. 1.6 g of **2** as colorless liquid was obtained in 22% yield.

*4.2.3. 2,2,3,4,4-Pentafluorobut-3-enenitrile (PFACN) (**2**)*

IR (Gas phase) ν (cm^{-1}) 2261 (C≡N), 1792 (C=C), 1371, 1164 (N≡C–C), 1123, 974; ^{13}C NMR (75.5 MHz, CD_3CN) δ 156.2 (tdt, $^1J_{CF}$ = 293 Hz, $^2J_{CF}$ = 39 Hz, $^3J_{CF}$ = 4 Hz), 123.6 (dm, $^1J_{CF}$ = 239 Hz), 110.8 (t, $^2J_{CF}$ = 45 Hz), 104.5 (dddt, $^1J_{CF}$ = 244 Hz, $^2J_{CF}$ = 31 Hz, $^3J_{CF}$ = 6 Hz, $^3J_{CF}$ = 6 Hz); ^{19}F NMR (282.4 MHz, CD_3CN): δ -89.4 (ddt, $^2J_{FF}$ = 50 Hz, $^3J_{FF}$ = 39 Hz, $^4J_{FF}$ = 8 Hz, =C*F*, 1F), -94.0 (ddd, $^4J_{FF}$ = 20 Hz, $^4J_{FF}$ = 8 Hz, $^3J_{FF}$ = 20 Hz, CF_2, 2F), -103.8 (ddt, $^3J_{FF}$ = 117 Hz, $^2J_{FF}$ = 50 Hz, $^4J_{FF}$ = 20 Hz, =C*F*, 1F), -192.2 (ddt, $^3J_{FF}$ = 117 Hz, $^3J_{FF}$ = 39 Hz, $^4J_{FF}$ = 20 Hz, =C*F*, 1F); GC–MS (EI, 70 eV): *m/z* (%) = 157 (M^+, 60), 138 (M^+-F, 20), 131 (M^+-CN, 88), 107 (M^+-CF_2, 100), 100 (C_2F_4, 5), 93 (CF_3, 17), 81 (C_2F_3, 10), 76 (CF_2CN, 20), 69 (CF_3, 100), 50 (CF_2, 8), 31 (CF, 35).

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