IONIC DIMERISATION OF TRIFLUOROPROPENENITRILE AND ITS ADDITION REACTIONS WITH METHYL TRIFLUOROPROPENOATE*

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Dimerisation of trifluoropropenenitrile (*I*) in the presence of potassium fluoride and tertiary amines afforded a mixture of stereoisomeric perfluoro-4-methyl-2-pentenedinitriles (*II*), higher-boiling compounds, and 2,3,3,3-tetrafluoropropanenitrile (*III*) which arises by proton transfer from the solvent molecule. Under optimum conditions, product *II* was obtained in about 50% yield. Reaction of the nitrile *I* with methyl trifluoropropenoate (*IV*) gave, besides the dimers *II* and *V*, the product of addition of the nitrile *I* to the propenoate, *IV*, *i.e.* methyl 4-cyanoperfluoro-2-pentenoate (*VI*), and the addition product of the propenoate *IV* to the nitrile *I*, *i.e.* methyl 4-cyanoperfluoro-2-methyl-3-butenoate (*VII*). The relative reactivity of *I* and *IV* is discussed. The ratio of stereoisomers in *II*, *V*, *VI* and *VII* indicates that the magnitude of the steric substituent effect, operating in the reaction mechanism, decreases in the order $—CFCF_3.(COOCH_3) > —CFCF_3(CN) > —COOCH_3 > —CN$.

Dimerisation and oligomerisation of fluorinated olefinic compounds have been extensively studied[1-6]. These reactions are catalysed with alkali metal fluorides[1-4], quaternary ammonium fluorides[1], tertiary amines[5] or triethanolamine[6,7]. The degree of oligomerisation can be controlled significantly by the reaction conditions. Derivatives of some unsaturated acids, such as methyl trifluoropropenoate[8,9], methyl perfluoro-2-methylpropenoate[10,11] or perfluoro-2-methylpropenenitrile[10,11], also undergo dimerisation. This paper concerns the study of dimerisation of trifluoropropenenitrile (*I*).

The results of dimerisation under various experimental conditions are given in Table I. In addition to a mixture of stereoisomeric perfluoro-4-methyl-2-pentenedinitriles (*II*), the reaction affords higher-boiling compounds and 2,3,3,3-tetrafluoropropanenitrile (*III*), which is formed as the side product by proton transfer from the solvent molecule to the intermediate carbanion *Ia*. The best medium for formation of the dimer *II* proved to be 1,2-dimethoxyethane and nitrobenzene with potassium fluoride as catalyst. The undesired derivative *III* was formed in all cases where the reaction mixture contained a compound with C—H bonds, not excepting nitro-

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TABLE I

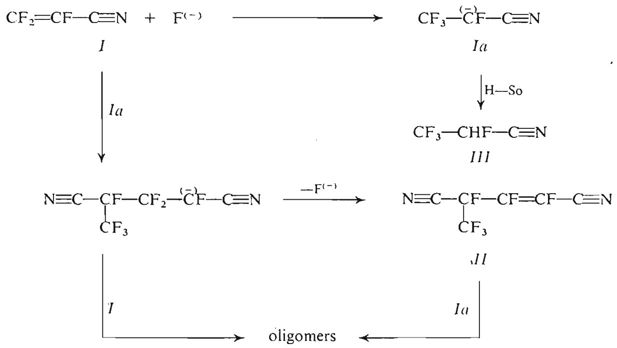
Dimerisation of Trifluoropropenenitrile (*I*)

Solvent	Catalyst	Nitrile g/mmol	Time h	Temperature °C	Product[a]			
					g	*I*[b]	*II*[b]	*III*[b]
Dimethylformamide	KF	3/28	5	20	0·6	—	42·6	57·4
Dimethylformamide[c]	KF	12/112	8	20	6·0	—	41·2	41·8
Hexamethyltriamidophosphate	KF	4/38	5	40	0·7	—	70·7	29·3
Tetrahydrothiophene 1,1-dioxide	KF	4/38	5	40	0·9	—	66·6	33·4
Tetrahydrothiophene 1,1-dioxide	KF	5/47	1·5	27	1,1	—	84·1	15·9
Dimethyl sulfoxide	KF	4/38	5	20	0·7	—	19·8	80·2
Diethylene glycol dimethylether	KF	5/47	4	18	1,2	—	55·2	34·4
Pentachlorotrifluoropropane *	KF	5/47	14	40	1·3	66·8	8·2	—
Pentachlorotrifluoropropane[c]	KF + CE[d]	12/112	8	20	3·2	—	64·6	15·0
Dibutyl ether	KF	5/47	14	20	1·4	60·4	29·4	10·2
1,2-Dimethoxyethane[c]	KF	10/93	8	—70—0	4·3	—	90·2	9·8
Acetonitrile[c]	KF	12/112	8	20	3·2	—	85·0	10·0
Acetonitrile	$(CH_3CH_2)_3N$	5/47	1	18	0·5	—	46·0	54·0
Acetonitrile	$(HOCH_2CH_2)_3N$	5/47	1	18	0·8	—	63·2	36·8
Nitrobenzene	KF	5/47	5	55	2·3	—	92·4	7·6
Nitrobenzene	KF	5/47	3	40	1·8	60·1	30·6	9·3
Nitrobenzene	$(CH_3CH_2)_3N$	3/28	0·5	17	0·4	15·4	61·2	23·4

[a] The difference between the starting amount and product weight is due to high-boiling compounds; [b] determined by gas–liquid chromatography without calibration (mean of two measurements, % rel.); [c] according to method *A* (see Experimental); [d] CE = 18-crown-6-ether.

benzene or 18-crown 6-ether. The greatest amount of *III* was formed in dimethylformamide and dimethyl sulfoxide with potassium fluoride as catalyst or in acetonitrile with triethylamine. In most cases the conversion of trifluoropropenenitrile was complete. Unidentified high-boiling compounds usually represented more than 50% (wt) of the reaction mixture; this portion corresponded to the difference between the original amount of trifluoropropenenitrile and the amount of isolated volatile products. Of the studied catalysts, potassium fluoride proved to be the best. On the other hand, triethylamine or triethanolamine, which have an effect similar to alkali metal fluorides[6], were less efficient in the dimerisation of trifluoropropenenitrile. The dimer *V*, arising from methyl trifluoropropenoate (*IV*), consisted of two configurational isomers whose ratio depended on the reaction conditions[9]. On the contrary, both the configurational isomers of the dimer obtained from trifluoropropenenitrile (*II*) were invariably present in approximately equimolecular amount.

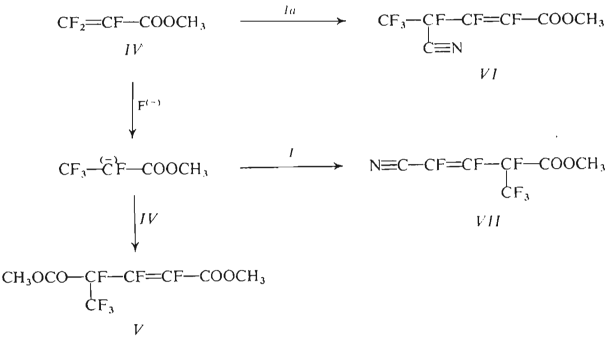
On the basis of the analogous dimerisation of methyl trifluoropropenoate (*IV*) we suggested the dimerisation mechanism for trifluoropropenenitrile (*I*) (Scheme 1). The dimerisation of this compound is substantially faster than that of the propenoate *IV* and affords a relatively great amount of high-boiling compounds which in all probability are oligomers of the nitrile I. This assumption is supported also by the fact that under dimerisation conditions the dimer *II* reacts with potassium fluoride and is transformed to high-boiling compounds. Therefore, the oligomers are probably formed by two pathways: either by a consecutive reaction from the dimer *II* or by by a "direct" oligomerisation of the nitrile *I*.



IIa = *cis-II*.; *IIb* = *trans-II*; H—So = Solvent

SCHEME 1

Derivatives of perfluoro-2-methylpropenoic[10,11] and perfluoropropenoic[9] acids are highly reactive under dimerisation conditions. The monomers[12,13] *I* and *IV* exhibit great affinity towards nucleophilic reagents[14–16] and trifluoropropenenitrile was shown[17] to be even more reactive. In connection with dimerisation studies we were interested whether the reactivity of compounds *I* and *IV*, which in the course of dimerisation add nucleophilic species, would be qualitatively preserved. Since the nitrile *I* boils below room temperature, we studied the overall reactivity by mutual addition reaction in an ampoule. Various molar ratios of both reactants were employed (Table II). We obtained products of the "individual" dimerisation *II* and *IV*, as well as products of the "crossed" addition, *i.e.* methyl 4-cyanoperfluoro-2-pentenoate (*VI*) and methyl 4-cyanoperfluoro-2-methyl-3-butenoate (*VII*), as depicted in Scheme 2.



SCHEME 2

TABLE II

"Crossed" Addition of Trifluoropropenenitrile (*I*) and Methyl Trifluoropropenoate (*IV*)

Molar ratio *I*/*IV* % rel.	Nitrile g/mmol	Ester g/mmol	Products[a]						
			g	*I*[b]	*II*[b]	*IV*[b]	*V*[b]	*VI*[b]	*VII*[b]
34/66	7·8/73	21/150	4·0	15·7	7·6	67·5	6·3	2·0	0·9
25/75	8·0/75	32/230	4·2	—	19·7	55·4	—	15·0	9·9
16/84	8·0/75	47/350	3·9	—	7·7	82·3	2·6	4·0	3·4

[a] Fraction boiling at 40 to 100°C/2·7 kPa; [b] determined by gas–liquid chromatography without calibration (mean of two measurements, % rel.).

We were not able to separate quantitatively the individual compounds *I* – *VII* from the solvent and therefore the composition of the isolated fraction (Table II) may not correspond to that of the reaction mixture. As comparable we consider the data on compounds *II*, *VI* and *VII* which have similar boiling points and at the same time their boiling points differ sufficiently from that of solvent. The percentages of the dimer *II* and of the adducts *VI* and *VII* are similar; this means that (with great excess of the propenoate *IV* in the reaction mixture) dimerisation of the nitrile *I* is substantially faster than its addition to the propenoate *IV* or its reaction with the intermediate *IVa*, derived from the propenoate *IV*. We tried to assess the relative reactivity of the compounds *I* and *IV* from the ratio of *II* and *VI* which arise in competitive reactions of the monomers *I* and *IV* with the intermediate *Ia*. For the individual experiments the ratio of reaction rates ranged from 4 to 10.

Monomers *I* and *IV* react smoothly with fluoride ion to give the intermediates *Ia* and *IVa*. On the basis of greater affinity of trifluoropropenenitrile towards nucleophiles[17] and its substantially higher dimerisation rate we assume that also its affinity towards fluoride ions is greater than that of the monomer *IV*. This conclusion is supported by data on the relative amount of the isomeric adducts *VI* and *VII*, the ratio of which varies only in a small range (70 : 30, 60 : 40, 53 : 47) with growing excess of the propenoate *IV* (1 : 2, 1 : 3, 1 : 5). We can therefore estimate that the dimerisation rates of the nitrile *I* and propenoate *IV* differ by a factor greater than ten.

We found previously[9] that in some solvents such as nitrobenzene, acetonitrile or diethylene glycol dimethyl ether no subsequent *cis-trans* isomerisation of the dimer *V* takes place and that (within the experimental error) in these solvents the ratio of configurational isomers is independent of solvent and temperature in the region 40 – 80°C. Also in this work we proved that, in nitrobenzene, the dimer *II* and the adducts *VI* and *VII* do not undergo any subsequent *cis-trans* isomerisation.

The *cis-trans* ratio in the products of dimerisation and "crossed" addition is given in Table III. From the results we can assess qualitatively the magnitude of steric substituent effect in the transition state as mentioned previously[9]. The ratio of con-

TABLE III

Percentage of Geometric Isomers (% rel.) in the Products of Dimerisation and "Crossed" Addition of Compounds *I* and *IV*

Compound	*II*	*V*	*VI*	*VII*
cis/trans-	50/50[a]	13/87[a]	22/73	40/60

[a] The same ratio found also in the preparative reaction.

figurational isomers in the products *VI* and *VII* indicates that also in "crossed" additions the steric effect of groups bonded to the double bond plays a dominant role. Dimerisation of trifluoropropenenitrile (*I*) affords an equimolecular mixture of configurational isomers as the result of a smaller steric bulk and rigidity of the CN group. In the case of the dimer *V*, where the more bulky groups $CFCF_3.(COOCH_3)$ and $COOCH_3$ can interact in the transition state[9], the *trans*-isomer highly predominates. The configurational isomers ratio in the product *VI* shows that the group $CFCF_3(CN)$ has a smaller effect than the $CFCF_3(COOCH_3)$ group. These results are further confirmed by the composition of the adduct *VII*. The operation of the steric substituent effect in the studied dimerisations and "crossed" additions

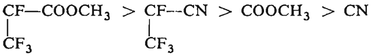
TABLE IV

NMR Spectra of Compounds *II*, *III*, *VI* and *VII*

Chemical shift, ppm (number of protons); s singlet, d doublet, q quartet, m multiplet; coupling constants J in Hz. ^{19}F NMR spectra related to CCl_3F.

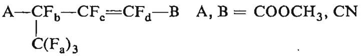
Compound	Spectrum	Signals
II	^{19}F	*cis*-isomer: m −170·3 (=CF_d—); ddq −169·1 (—CF_c=), $^{3}J_{F_cF_d}$ = 26·0; dq −121·1 (—CF_b—), $^{3}J_{F_bF_c}$ = 19·0, $^{3}J_{F_bF_d}$ = 7·0; dd −78·3 (CF_a—), $^{3}J_{F_aF_b}$ = 12·0, $^{3}{}_{F_aF_c}$ = 6·0; *trans*-isomer: ddm −152·6 (—CF_d—); ddq −141·5 (—CF_c=), $^{3}J_{F_cF_d}$ = 141·0; d −133·6 (—CF_b—); q −77·8 (CF_a—), $^{3}J_{F_aF_b}$ = 12·0
III	^{1}H	dq (1) 7·25, $^{2}J_{HF}$ = 45·0, $^{3}J_{HF}$ = 9·0
	^{19}F	m −203·0 (—CF—); q −77·8 (CF_3—), $^{3}J_{FF}$ = 15·0
VI	^{1}H	double singlet 1 : 1 3·86 and 3·94
	^{19}F	*cis*-isomer: dq −155·8 (=CF_d—); dq −154·2 (—CF_c=), $^{3}J_{F_cF_d}$ = 20·0; m −139·5 (—CF_b—), $^{3}J_{F_bF_c}$ ~ 5; m −78·5 (CF_a—), $^{3}J_{F_aF_b}$ ~ 15; *trans*-isomer: dd −130·5 (—CF_b—); m −122·8 (=CF_d—); m −121·7 (—CF_c—), $^{3}J_{F_cF_d}$ = 125·0; m −76·3 (CF_a—), $^{3}J_{F_aF_b}$ = 10·0
VII	^{1}H	double singlet 1 : 1 3·89 and 3·92
	^{19}F	*cis*-isomer: m −172·4 (=CF_d—); m −169·8 (—CF_c=), $^{3}J_{F_cF_d}$ 35·0; dqd −135·3 (—CF_b—), $^{3}J_{F_bF_c}$ 20·0; dd −76·9 (CF_a—), $^{3}J_{F_aF_b}$ = 15·0, $^{3}J_{F_aF_c}$ = 15·0; *trans*-isomer: q −159·6 (—CF_b—); dm −148·3 (=CF_d—); dm −144·5 (—CF_c=), $^{3}J_{F_cF_d}$ = 125·0, $^{3}J_{F_bF_c}$ ~ 5; m −75·6 (CF_a—), $^{3}J_{F_aF_b}$ = 15·0

also indicates that the formation of compounds *II*, *V*–*VII* in the rate-determining step is kinetically controlled[9], in accord with previous mechanistic conclusions[9]. Following order of the steric substituent effect in dimerisations and "crossed" additions can be derived from Table III:



$$\underset{\displaystyle \mathrm{CF_3}}{\mathrm{CF}}\text{—}\mathrm{COOCH_3} > \underset{\displaystyle \mathrm{CF_3}}{\mathrm{CF}}\text{—}\mathrm{CN} > \mathrm{COOCH_3} > \mathrm{CN}$$

Structure of compounds *II*, *VI* and *VII* was determined by NMR (Table IV), IR (Table V) and mass (compound *II*) spectra and elemental analyses. We were not able to separate the configurational isomers of *II*, *VI* and *VII*; they were identified in the diastereoisomeric mixtures by ^{19}F-NMR spectra on the basis of chemical shifts and coupling constants in the model *VIII*.



$$\mathrm{A}\text{—}\underset{\displaystyle \mathrm{C(F_a)_3}}{\mathrm{CF_b}}\text{—}\mathrm{CF_c}{=}\mathrm{CF_d}\text{—B} \quad \mathrm{A, B} = \mathrm{COOCH_3, CN}$$

VIII

TABLE V

IR Absorption Maxima of Products *II*, *III*, *VI* and *VII* (600—1 000 cm^{-1} in CS$_2$, 1 000—4 000 cm^{-1} in CCl$_4$)

Compound	ν(C=C)	ν(C=O)	ν(C≡N)	Other maxima
II	1 702 w	—	2 260 w 2 270 w	850 w, 868 w, 895 m, 1 023 s, 1 114 m, 1 130 m, 1 145 s, 1 193 s, 1 235 s, 1 265 s, 1 310 m
III	—	—	2 280 w	720 m, 1 104 m, 1 165 s, 1 204 s, 1 275 s, 1 357 m, 2 960 w
VI	1 695 w	1 765 s 1 772 m	2 270 w	905 w, 965 m, 1 032 m, 1 154 m, 1 235 s, 1 263 s, 1 295 m, 1 348 m, 1 443 m, 2 860 w, 2 970 w
VII	1 698 w	1 786 s 1 798 m	2 250 w	812 w, 965 m, 1 021 m, 1 090 m, 1 140 m, 1 185 m, 1 220 s, 1 253 s, 1 290 m, 1 372 w, 1 443 m, 2 860 w, 2 970 w

EXPERIMENTAL

The temperature data are uncorrected. Gas–liquid chromatography was performed on Chrom 3 and Chrom 41 instruments (Laboratorní přístroje, Prague; flame ionisation detector, column diameter 0·6 or 0·3 cm, carrier gas nitrogen; support Chromaton N-AW-DMCS, Lachema, Brno). Preparative gas–liquid chromatography was carried out on a modified Chrom 2 instrument (flame ionisation detector, column diameter 1 cm, length 500 cm). The IR spectra were recorded on a Perkin–Elmer 325 (Bodenseewerk) instrument, NMR spectra were taken on a Varian XL-100-15 (Palo Alto) spectrometer in deuteriochloroform. The mass spectra were measured on a one focus LKB 9000 Gas Chromatograph — Mass Spectrometer (Stockholm); 70 eV, chromatographic separation on poly(ethyleneglycol adipate), carrier gas helium.

Chemicals: Trifluoropropenenitrile (*I*) and methyl trifluoropropenoate (*IV*) were prepared according to the previously described procedures[18,19]. Potassium fluoride (Lachema, Brno) was dried at 120°C and 1·33 Pa (0·01 Torr). The potassium fluoride used in the reaction was weighed in dry atmosphere. Solvents were purified and dried according to ref.[20,21].

Dimerisation of Trifluoropropenenitrile

A. *Under atmospheric pressure.* Gaseous trifluoropropenenitrile was introduced at 20°C in a stream of nitrogen into a stirred mixture of potassium fluoride (1 g; 17·5 mmol) and the appropriate solvent (25 ml) (Table I). After removal of the catalyst by filtration, the mixture was distilled at 2·7 kPa (20 Torr) and the products were trapped in a receiver, cooled with dry ice. Redistillation afforded a mixture of perfluoro-4-methyl-2-pentenedinitrile (*II*) and 2,3,3,3-tetrafluoropropenenitrile (*III*) which were separated by preparative gas-liquid chromatography (stationary phase Carbowax 6000, 70°C).

B. *Under elevated pressure.* A mixture of catalyst (1 g), solvent (30 ml) and trifluoropropenonitrile was heated and shaken in a glass ampoule (Table I). The reaction mixture was distilled at 2·7 kPa (20 Torr) and the products isolated analogously as described under *A*. For NMR and IR spectra of the products see Table IV and V. Mass spectra: Dimer *II*: 214/1 $(M)^+$, 194/6 $(M-F)^+$, 145/7 $(M-CF_3)^+$, 138/9 $(C_4F_4N)^+$, 100/34 $(C_2F_4)^+$, 93/12 $(C_3F_3)^+$, 81/13 $(C_2F_3)^+$, 69/100 $(CF_3)^+$, 62/10 $(C_2F_2)^+$, 50/16 $(CF_2)^+$, 31/88 $(CF)^+$; compound *III*: 127/1 $(M)^+$, 108/65 $(M-F)^+$, 69/100 $(CF_3)^+$, 50/11 $(CF_2)^+$, 32/11 $(CHF)^+$, 31/62 $(CD)^+$. *II*: For $C_6F_6N_2$ (214·0) calculated: 33·66% C, 53·25% F, 13·09% N; found: 33·80% C, 52·98% F, 13·22% N. *III*: For C_3HF_4N (127·0) calculated: 28·86% C, 0·79% H, 59·86% F, 11·03% N; found: 28·23% C, 1·04% H, 60·02% F, 10·71% N.

C. *Preparative reaction.* A mixture of potassium fluoride (5 g; 87·5 mmol), nitrobenzene (150 ml) and nitrile *I* (20 g; 0·187 mol) was heated (according to the method *B*) for 2·5 h at 75°C and then distilled at 2·7 kPa. The products were collected in a receiver cooled with dry ice. Fractionation afforded 10·2 g (47·6 mmol) of the dimer *II*, boiling at 90—94°C; yield 50·1%, 98·5% purity (gas-liquid chromatography on Carbowax 6000 at 86°C).

Addition of Trifluoropropenenitrile (*I*) and Methyl Trifluoropropenoate (*IV*)

A mixture of potassium fluoride (3 g; 52 mmol), nitrobenzene (150 ml), the nitrile *I* and the acrylate *IV* was shaken in a glass ampoule for 2·5 h at 70°C, distilled at 2·7 kPa and the fraction b.p. 40—100°C collected. The reaction products were first chromatographically analysed (Table II) and then combined and redistilled. The adducts *VI* and *VII* were separated by preparative gas–liquid chromatography (15% poly(butanediol succinate), 40°C, 6°C/min), affording 1·2 g (5 mmol) of methyl 4-cyanoperfluoro-2-pentenoate (*VI*) and 0·73 g (3 mmol) of methyl 4-cyanoperfluoro-2-methyl-3-butenoate (*VII*). For the NMR and IR spectra of the products see Tables IV and V. For $C_7H_3F_6NO_2$ (247·0) calculated: 34·01% C, 1·21% H, 46·15% F, 5·66% N; for *VI* found: 33·65% C, 1·36% H, 45·87% F, 5·43% N; for *VII* found: 33·72% C, 1·38% H, 46·12% F, 5·38% N.

Spectral measurements were carried out in the Department of NMR *Spectroscopy (Dr P. Trška, Head), in the Department of Mass Spectrometry (Dr V. Kubelka, Head) and in the Department of* IR *Spectroscopy (Dr A. Muck, Head); elemental analyses were performed in the Department of Organic Analysis (Dr L. Helešic, Head), all of the Institute of Chemical Technology, Prague. This help is gratefully akcnowledged.*

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