DERIVATIVES OF 2,3-DIFLUORO-2-BUTENEDIOIC ACID AND THEIR ISOMERIZATION REACTIONS*

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The vinylic nucleophilic substitution of methyl trifluoropropenoate (*I*) with potassium cyanide affords methyl 2,3-difluoro-3-cyanopropenoate (*II*) in the form of a mixture of *cis*- and *trans*-isomers in 95 : 5 ratio. Simultaneously the dimerization of propenoate *I* to dimethyl perfluoro-4-methyl-2-pentenedioate (*III*) also takes place to a lesser extent. On acid catalysed methanolysis of compound *II* dimethyl 2,3-difluoro-2-butenedioate (*VI*) is formed with the same content of configurational isomers. Diester *VI* with a relative *cis* : *trans* ratio of 35 : 65 was obtained on dehalogenation of dimethyl 2,3-dichloro-2,3-difluorobutanedioate (*V*), which was prepared by addition of chlorine to the cyano derivative *II* and subsequent acid catalyzed methanolysis. When reacting them with potassium fluoride in dimethyl sulfoxide compounds *II* and *VI* underwent anionic *cis-trans* isomerization reaction. In the 0---80°C interval the *cis* isomers prevail in the equilibrium mixture, and the conversion *cis*→*trans* is endothermic: in the 40---80°C interval for $IIa{\rightarrow}IIb$ $\Delta H = 12\cdot8$ kJ mol^{-1}, for $VIa{\rightarrow}VIb$ $\Delta H = 38\cdot6$ kJ mol^{-1}. The influence of the *cis*-effect of the fluorine atoms on the thermodynamic stability of the configurational isomers of compounds *II* and *VI* is discussed.

Perfluoroolefins[1,2] with a terminal double bond and perfluoropropenoates[3-5] undergo dimerization in the presence of the reagents which afford fluoride ion. In contrast to this, dimethyl perfluoro-4-methyl-2-pentenedioate (*III*) does not undergo dimerization, while in dipolar aprotic solvents its anionic *cis-trans* isomerization takes place[6]. The equilibrium content of configurational isomers is temperature dependent in a peculiar manner, which is either a phenomenon specific for compound *III* alone, or it may represent a characteristic property of the group of perfluorinated unsaturated esters containing two vicinal fluorine atoms on the double bond within the chain. The simplest representative of the group of substances mentioned is dimethyl 2,3-difluoro-2-butenedioate (*VI*) or methyl 2,3-difluoro-3-cyanopropenoate (*II*) which we have used for study in this paper.

Difluoro-2-butenedioic acid was prepared for the first time[7,8] from chlorotrifluoroethene and 1,1-dichloroethene; this route was later replaced by fluorination of the derivatives of dichloro-2-butenedioic acid with alkali fluorides[9,10] at elevated

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temperatures or by fluorination with mercuric fluoride[11]. Oxidation[12] of perfluoro-phenols with peracids gives difluoro-2-butenedioic acid in one step, the same as the pyrolysis[13] of halogenofluoroacetonitriles.

In this study we tried to make use of the reactivity of methyl trifluoropropenoate (I) and trifluoropropenenitrile in nucleophilic additions[14] and to react these compounds with the cyanide ion in order to obtain derivatives of difluoro-2-butenedioic acid. From earlier results it follows that the highly fluorinated ethenes and perfluoro-propene react with alkali cyanides[15-20] under formation of various products. The addition of the cyanide ion to fluorinated olefins in aprotic solvents containing water[15,16] always afforded a mixture of the saturated acid and its amide, while in weakly protic medium[17] the formation of unsaturated fluorinated nitriles took place. In this paper the reaction of propenoate I with potassium cyanide in anhydrous acetonitrile gave a mixture of two products, cyano derivative II and pentenedioate III. Compound II was formed on vinyl substitution of the fluorine atom, which in halo-genated ethenes usually takes place[18-20] by an addition-elimination mechanism, comprising the addition of the nucleophilic species under formation of the carba-nionic intermediate (Ia) and the elimination of the halogenide ion (Scheme 1). Compound III is a product of the dimerization reaction[5] of ester I and its formation indicated the presence of alkaline fluoride in the reaction mixture. In our effort
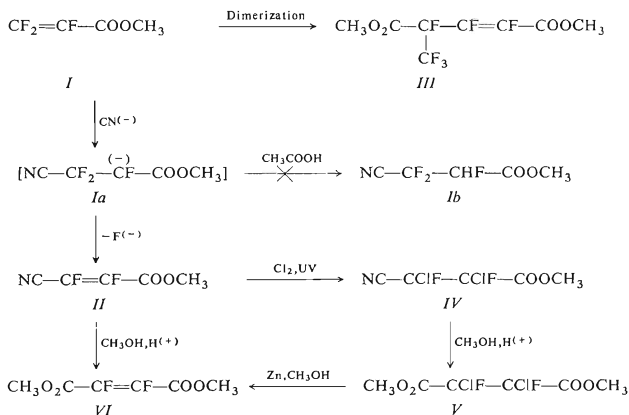

IIa, VIa, cis
IIb, VIb, trans

SCHEME 1

to prevent the elimination of the fluoride ion from the intermediate Ia and so to suppress the undesirable dimerization reaction by addition of a source of protons in the reaction mixture, we carried out the reactions with potassium cyanide in the presence of acetic acid. However, the ratio of compounds II and III remained without pronounced changes. In addition to this we were unable to detect the formation of compound Ib. In contrast to this temperature had a considerable effect on the relative amount of the final compounds II and III; while dimerization was the main reaction at $20-25°C$, substitution dominated at $-10°C$. In attempts at the preparation of cyano derivative of trifluoropropenenitrile dimerization of the starting compound was observed even at low temperatures.

Cyano derivative II is formed as a mixture of cis- (IIa) and trans-isomer (IIb) in a 95 : 5 ratio. The dimer III contained $4·2\%$ of the cis- and $95·8\%$ of the trans-isomer, i.e. within the limits of the experimental error, as observed earlier[5]. Under the conditions of the reaction with the cyanide ion, cis-trans isomerization of products II and III does not take place, from which it follows that the ratio of the configurational isomers is the result of a mechanism of a substitution or dimerization reaction resp. The intermediate Ia is stabilized[6,21,22] by the conjugation with the methoxycarbonyl group, and for this reason it probably has a planar arrangement on the carbanionic carbon atom. The conformation of the carbanion Ia, very close to the transition state[23] (Ic,Id), is shown in Scheme 2. For a possible anti- (Ic) or syn-elimination (Id) the groups CN and COOCH$_3$ are in synclinal conformation. In a similar
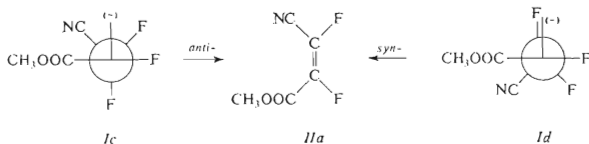
SCHEME 2

elimination of the fluoride ion we found[24] that the effect of the steric hindrance of the CN group is relatively small. The configurational composition of the product II, formed by the addition-elimination reaction mentioned, at $-10°C$, i.e. 95% cis- and 5% trans-isomer, is within the experimental error range, the same as the composition of the equilibrium mixture obtained at $0°C$ ($94·4\%$ cis- and $4·6\%$ trans-isomer),

Applying acid-catalyzed methanolysis onto cyano derivative II we obtained diester VI with the same proportion of the configurational isomers as in the starting compound II. Aiming to obtain compound VI with a different ratio of configurational isomers we carried out its synthesis by dehalogenation. Cyano derivative II served as starting compound which was converted to methyl 2,3-dichloro-2,3-di-

fluoro-3-cyanopropanote (*IV*) by addition of chlorine under irradiation with ultra-violet light. This compound was submitted to acid-catalyzed methanolysis to yield dimethyl 2,3-dichloro-2,3-difluorobutanedioate (*V*), which was dehalogenated with zinc in methanol to diester *VI*. In the product *VI* the *trans*-isomer prevailed in a 65 : : 35 ratio.

The structure of compounds *II* − *VI* was determined on the basis of infrared, mass (compound *II* and *VI*) and NMR spectra (Table 1), as well as elemental analyses. We were not able, however, to separate the configurational isomers of compounds *II* and *VI*. Their structure was determined on the basis of the chemical shifts and the coupling constants in the ^{19}F-NMR spectrum. As was said earlier[25,26], in 1,2-di-fluoro-olefins and their analogues with a *trans*-configuration of the fluorine atoms the coupling constant $^3J_{FF}$ is always higher than in olefins with a *cis*-configuration of the fluorine atoms. In substituted *cis*-1,2-difluoroethenes the coupling constant $^3K_{FF}$ range is between 8 − 36 Hz, while in *trans*-1,2-difluoroethenes it is within the 129 − 142 Hz range. Hence, substances with a coupling constant lower than 8 Hz and higher than 120 Hz may be unambiguously assigned the *cis*- or the *trans*-con-figuration of the fluorine atoms on the double bond. We determined the structure of compound *II* by assigning the signals of the fluorine atoms split with a coupling constant $^3J_{FF} = 3$ Hz the configuration *cis* and the signals of the fluorine atoms

TABLE I

NMR Spectra of Compounds *II*, *IV—VI*

Chemical shifts in ppm (number of protons); s singlet, d doublet; coupling constants *J* in Hz. ^{19}F-NMR spectra referred to CCl$_3$F.

Compound	Type of spectrum	Character of the signals
II	^{1}H	s(3) 3·96
IIa	^{19}F	*cis*-isomer: d-135·0, d-124·9 $^3J_{FF} = 3·0$
IIb	^{19}F	*trans*-isomer: d-147·7, d-144·9 $^3J_{FF} = 136·0$
IV	^{1}H	s(3) 4·00
	^{19}F	d-111·1, d-116·3 $^3J_{FF} = 20·0$
V	^{1}H	double singlet 1 : 1 3·94 and 3·90
	^{19}F	d-124·4, d-117·1 $^3J_{FF} = 5·0$
VI	^{1}H	s(3) 3·88
VIa	^{19}F	*cis*-isomer: d-137·5 $^3J_{FF} = 8·0$
VIb	^{19}F	*trans*-isomer: d-146·2 $^3J_{FF} = 130·0$

with $^3J_{FF} = 136$ Hz the configuration *trans*. Analogously, in the case of compound *VI*, the signals of the fluorine atoms with the coupling constant $^3J_{FF} = 8$ Hz the configuration *cis* was assigned and the signals with the coupling constant $^3J_{FF} = 130$ Hz the configuration *trans*. The content of the configurational isomers in compounds *II* and *VI* was determined from the integral intensities of the fluorine atom signals in the ^{19}F-NMR spectrum.

The nitrile and the esters of trifluoropropenoic acid undergo dimerization and mutual additions in the presence of potassium fluoride in suitable solvents and also without diluents[5,24]. Under the same conditions neither the cyano ester *II* nor the diester *VI* undergo dimerization reaction. Under the catalytic effect of potassium fluoride only *cis-trans*-isomerization takes place. When comparing compounds *II* and *VI*, or *III* (see ref.[6]) in this respect with the models in the perfluoro-2-alkene series, for example with perfluoro-2-butene[1,27], perfluoro-3-methyl-2-pentene[1,27] and perfluoro-4-methyl-2-pentene[1,28], it may be seen that they do not undergo isomerization either (perfluoro-2-butene only to a certain extent, but under much more vigorous conditions[29]) but that they do react[1,2] by addition with carbanions which are formed on reaction of the fluoride ion with perfluoroolefins containing a terminal double bond. It seems to be a rule that perfluorinated olefins and substances such as esters and nitriles of perfluoroalkenoic and perfluoroalkenedioic acid, containing a double bond within the chain, do not dimerize at all or with great difficulty, since they do not form a sufficiently reactive carbanion on reaction with the fluoride ion. We tried to prove the existence of a carbanion of the type *Ia* in the reaction of diester *VI* with potassium fluoride using methyl iodide as in ref.[30], but we were unable to identify the product of the assumed substitution. In this reaction diester *VI* reacts easily with sodium methoxide in methanol under formation of dimethyl 2-fluoro-3-methoxy-2-butenedioate[31].

We carried out the isomerization reaction[6] of compounds *II* and *VI* in dimethyl sulfoxide, similarly as in the case of dimer *III*, when we demonstrated that it is a heterogeneously catalyzed reaction. The isomerization was carried out till the equilibrium was attained and we also investigated the temperature dependence of the equilibrium composition (Fig. 1). From this figure it follows that in the $0-80°C$ interval the *cis*-isomer (*IIa*, *VIa*) strongly predominates in the equilibrium mixtures, and that its content decreases with increasing temperature. Hence, the conversion *cis→trans* is in both substances, *II* and *VI*, endothermic. In the $40-80°C$ interval the reaction enthalpy of the conversion *IIa→IIb* $\Delta H = 12.8$ kJ mol^{-1}, and of the conversion *VIa→VIb* $\Delta H = 38.6$ kJ mol^{-1} (determined graphically), *i.e.* the *cis*-isomers are thermodynamically more stable. From these and the preceding results[6] it may be judged that the relative stability of the configurational isomers of compounds *II*, *III* and *VI* is affected by the non-bonding and bonding interactions of the substituents on the double bond. Among non-bonding interactions primarily the steric hindrance should be considered, which makes the *trans*-isomers, as a rule,

energetically poorer[32] and thus also the prevailing configuration. For example an equilibrium mixture of *cis-* and *trans*-dimethyl 2-butenedioate[33] contains the *trans*-isomer exclusively within a broad temperature range (102°C — 98·5%, 240°C — 82·7%). In comparison with this substance it is evident that the stability of the configurational isomers in derivatives *II* and *VI* of the difluoro-2-butenedioic acid is mainly affected by the bonding interaction of the substituents. Among them belongs the so-called *cis*-effect of the fluorine substituents, which makes, for example, *cis*--1,2-difluoroethene more stable than its *trans*-isomer[34−36]. A similar, but weaker effect is also exhibited by chlorine and bromine[37]. Steric hindrance of other groups on the double bond contributes to this effect, which acts in the opposite manner[3] and which should be more pronounced in diester *VI*. Therefore we expected that about 0°C, when the curves in Fig. 1 have an approximately zero derivation, the proportion of the isomer *VIa* would be smaller than of the isomer *IIa*. However, in fact the opposite is true and from this discrepancy we consider that the thermodynamic stability of the mentioned configurational isomers is affected by further interactions, for example between the fluorine atoms and other substituents on the double bond, or between the substances and the solvent.

EXPERIMENTAL

The temperature data are not corrected. Gas chromatography was carried out on a Chrom 3 and Chrom 41 chromatographs (Laboratorní přístroje, Prague; FID, column diameter 0·6 and 0·3 cm, integrator, carrier of the stationary phase Chromaton N-AW-DMCS, Lachema Brno). The infrared spectra were measured on a Perkin–Elmer 325 instrument (Bodenseewerk). The NMR spectra were recorded with a Varian XL-100-15 instrument (Palo Alto, deuteriochloroform, in the case of ^{19}F-NMR with respect to CCl_3F). The mass spectra were measured on a Gas Chromatograph-Mass Spectrometer tandem, LKB 9000 (Stockholm; single focus, energy of the electrons 70 eV, chromatographic inlet *via* poly(ethylene glycol adipate), carrier gas helium).
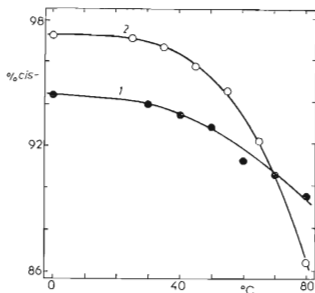

Fɪɢ. 1

Temperature Dependence of the Equilibrium Content of the *cis*-Isomer

1 IIa; 2 VIa.

Methyl trifluoropropenoate (*I*) was prepared and potassium fluoride and the solvents were dried as in the preceding paper[6]. Potassium cyanide (Lachema) was dried at 120°C and 1·33 Pa for 4 h.

Methyl 2,3-Difluoro-3-cyanopropenoate (*II*)

A mixture of propenoate *I* (100 g; 0·772 mol), potassium cyanide (60·2; 0·925 mol), acetic acid (40·3 g; 0·672 mol) and acetonitrile (300 ml) was stirred at —10°C for 6 h, then diluted with icy water (500 ml), washed with trichlorofluoromethane (200 ml) and dried over magnesium sulfate. After elimination of the solvent and rectification under reduced pressure 23·0 g (0·157 mol) of compound *II* were obtained, b.p. 83—86°C/10·6 kPa. Purity 95%, conversion 29%, yield 70·0%. The second product obtained by rectification was dimethyl perfluoro-4-methyl-2-pentene-dioate (*III*), yield 11·3 g (0·04 mol), b.p. 95—99°C/2·66 kPa, yield 11·3%. Gas chromatography on poly(butanediol succinate), 150°C. For the NMR spectrum of compound *II* see Table I. Infrared spectrum of compound *II* (tetrachloromethane, cm^{-1}): 932 w, 1038 s, 1050 s, 1183 s, 1210 s, 1255 s, 1272 m, 1348 s, 1444 s, 1680 s, 1718 m, 1760 s, 2250 w, 2865 w, 3020 w. Mass spectrum of *II*: 147/29 M^+, 116/100 $(M—OCH_3)^+$, 88/48 $(M—C_2H_3O_2)^+$, 69/10 C_3FN^+, 62/7 $C_2F_2^+$, 59/68 $(C_2H_3O_2)^+$, 31/68 $(CH_3O)^+$. For $C_5H_3F_2NO_2$ (147·1) calculated: 40·80% C, 2·05% H, 25·57% F, 9·54% N; found: 40·51% C, 2·78% H, 25·85% F, 8·97% N.

Methyl 2,3-Dichloro-2,3-difluoro-3-cyanopropanoate (*IV*)

A mixture of propenoate *II* (33·2 g; 0·226 mol) and 1,1,2-trichloro-trifluoroethane (100 ml) was chlorinated under irradiation with a mercury discharge lamp (Tesla, RVK 125 W) through a Pyrex filter, until conversion was 90% (gas chromatography on poly(propanediol sebacate), 150°C). The mixture was washed with a sodium sulfite solution (10%) and water, and dried over an-hydrous magnesium sulfate. Distillation under reduced presure yielded 29·8 g (0·137 mol) of *IV*, b.p. 72—76°C/3·3 kPa, purity 98%, preparative yield 67·5%. For the NMR spectrum of com-pound *IV* see Table I. Infrared spectrum of *IV* (tetrachloromethane, cm^{-1}): 750 s, 822 s, 990 s, 1002 s, 1025 s, 1130 s, 1170 s, 1248 s, 1267 s, 1348 m, 1445 m, 1445 m, 1792 s, 1805 s, 2626 w, 2850 w, 2960 w, 2992 w. For $C_5H_3Cl_2F_2NO_2$ (218·0) calculated: 27·55% C, 1·39% H, 32·53% Cl, 17·43% F, 6·43% N; found: 28·03% C, 1·41% H, 32·11% Cl, 16·94% F, 6·28% N.

Dimethyl 2,3-Dichloro-2,3-difluorobutanedioate (*V*)

A mixture of propanoate *IV* (29·8 g; 0·137 mol) methanol (42·5 g; 1·37 mol) and sulfuric acid (18·4 g; 0·187 mol) was refluxed for 15 h, then diluted with trichlorofluoromethane (100 ml), washed with icy water, potassium hydrogen carbonate (10%) and water, and dried over anhydrous magnesium sulfate. Distillation under reduced pressure gave 22·4 g (0·089 mol) of compound *V*, b.p. 114—118°C/3·72 kPa, purity 96%, yield 63·5%. For the NMR spectrum of compound *V*, see Table I. Infrared spectrum of *V* (tetrachloromethane, carbon disulfide, cm^{-1}): 684 m, 721 m, 760 m, 788 w, 841 w, 880 w, 955 m, 975 s, 1021 m, 1034 m, 1136 s, 1285 s, 1441 s, 1765 s, 1778 s, 2835 w, 2970 m, 3010 w. For $C_6H_6Cl_2F_2O_4$ (251·0) calculated: 28·71% C, 2·41% H, 28·25% Cl, 15·14% F; found: 29·35% C, 2·55% H, 27·76% Cl, 15·24% F.

Dimethyl 2,3-Difluoro-2-butenedioate (*VI*)

A) A mixture of diester *V* (2·5 g; 10 mmol), zinc (3·0 g; 46 mmol) and methanol (5 ml) was refluxed for 0·5 h and filtered. Distillation of the filtrate under reduced pressure afforded 0·76 g

(4·2 mmol) of *VI*, b.p. 82—89 C/2 kPa, yield 42%, in the form of a mixture of *cis* and *trans* isomers in a 35 : 65 ratio (gas chromatography on poly(butanediol succinate), 175°C).

B) A mixture of ester *II* (17·2 g; 0·117 mol), methanol (37·5 g; 1·17 mol) and sulfuric acid (16·8 g; 0·172 mol) was refluxed for 24 h, diluted with 200 ml of trichlorofluoromethane, washed with icy water, potassium hydrogen carbonate solution (10%) and water, and dried over anhydrous magnesium sulfate. Distillation under reduced pressure gave 11·5 g (0·064 mol) of *VI*, b.p. 72—82°C/2·26 kPa, purity 93%, yield 54·7% of a mixture of *cis* and *trans* isomers in a 95 : 5 ratio (gas chromatography on poly(butanediol succinate) at 175°C). For the NMR spectrum of compound *VI* see Table I. Infrared spectrum of *VI* (tetrachloromethane, cm^{-1}): 825 m, 918 w, 961 w, 1040 s, 1133 s, 1197 m, 1213 m, 1320 s, 1340 s, 1440 s, 1692 m, 1755 s, 2860 w, 2968 m, 3010 w. Mass spectrum of compound *VI*: *cis*-isomer: 180/14 M$^+$, 149/100 (M—CH$_3$O)$^+$, 121/11 (M—C$_2$H$_3$O$_2$)$^+$, 90/11 C$_3$F$_2$O$^+$, 71/10 C$_3$H$_3$O$_2^+$, 62/15 C$_2$F$_2^+$, 59/52 C$_2$H$_3$O$_2^+$, 31/15 CH$_3$O$^+$; *trans*-isomer: 180/15 M$^+$, 149/100 (M—CH$_3$O)$^+$, 121/18 (M—C$_2$H$_3$O$_2$)$^+$, 90/10 C$_3$F$_2$O$^+$, 71/8 C$_3$H$_3$O$_2^+$, 62/11 C$_2$F$_2^+$, 59/41 C$_2$H$_3$O$_2^+$, 31/12 CH$_3$O$^+$. For C$_6$H$_6$F$_2$O$_4$ (180·1) calculated: 40·02% C, 3·36% H, 21·10% F; found: 39·89% C, 3·57% H, 20·64% F.

cis-trans-Isomerization of Methyl 2,3-Difluoro-2-cyanopropenoate (*II*)

A mixture of potassium fluoride (1·6 g; 28 mmol), propenoate *II* (3·0 g; 20 mmol) (*cis-/trans-* = = 95 : 5) and dimethyl sulfoxide (20 ml) was stirred in a dry atmosphere at a given temperature so that the solid phase should remain dispersed. At 2 h intervals 2·5 ml of the solution were withdrawn which were diluted with 10 ml trichlorofluoromethane, washed with icy water and dried over anhydrous magnesium sulfate. Distillation under reduced pressure gave a sample of a mixture of the configurational isomers of substance *II*, the ratio of which was determined from the integral intensities of the fluorine atoms in the ^{19}F-NMR spectrum. The samples were withdrawn until the results of two subsequent determinations did not differ by less than 3% rel.

cis-trans-Isomerization of Dimethyl 2,3-Difluoro-2-butenedioate (*VI*)

A mixture of potassium fluoride (1·5 g; 26 mmol), butenedioate *VI* (2·7 g; 15 mmol) (*cis-/trans-* = = 95 : 5 or 35 : 65) and dimethyl sulfoxide (20 ml) was stirred as in the preceding experiment. The samples withdrawn were analysed immediately by gas chromatography (on poly(propanediol sebacate), column length 250 cm, 180°C, integrator) and the content of configurational isomers of compound *VI* determined. The samples were withdrawn until the results of two consecutive determinations did not differ by less than 3% rel.

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