IONIC DIMERISATION OF METHYL TRIFLUOROPROPENOATE*

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Dimerisation of methyl trifluoropropenoate (*I*) in solvents in the presence of potassium fluoride affords stereoisomeric dimethyl perfluoro-(4-methyl-2-pentene)dioates (*III*), the ratio of which depends on the reaction conditions. The reaction is accompanied by formation of methyl 2,3,3,3-tetrafluoropropenoate (*IV*), arising by proton transfer from the solvent to the carbanionic intermediate. Under suitable conditions complete conversion of the propenoate can be achieved and the dimer is obtained in 80—90% yield. Principal steps of the dimerisation were proved and the formation of configurational isomers is discussed in terms of kinetically controlled reaction.

Dimerisation and oligomerisation of perfluorinated olefinic compounds by the action of fluoride-ion-donating agents are known and recently extensively studied reactions[1-6]. Aliphatic as well as alicyclic[1-6] olefins undergo dimerisation; also perfluoro-methylenecyclopropane[7,8] affords a dimer. Recently, dimerisation reaction was observed with esters and nitriles derived from trifluoropropenoic[9-11] and perfluoro-2-methylpropenoic[12,13] acids. Dimerisation of methyl trifluoropropenoate (*I*) was observed first in the presence of cesium fluoride in ethylene glycol dimethyl ether[9], then in a mixture of potassium fluoride and nitromethane[10] and it was also found to be a side reaction in the irradiation of *I* in formamide[11]. The dimerisation of derivatives of perfluorinated unsaturated acids affords easily difunctional derivatives which cannot practically be prepared by other synthetic procedures. We have now studied dimerisation of methyl trifluoropropenoate[14-16] (see also ref.[17]) in the presence of potassium fluoride and the effect of solvents in this reaction.

The dimerisation took place without, as well as in the presence, of solvents. The dimer, dimethyl perfluoro-(4-methyl-2-pentene)dioate (*III*), invariably represented a mixture of configurational isomers. Spontaneous dimerisation without solvent after five hours afforded predominantly the *trans*-isomer *IIIb*. Controllable reaction was achieved in aprotic solvents (Table I). Surprisingly, although with low conversion, the compound reacted also in tert-butyl alcohol which, unlike primary and secondary alcohols, does not add[18] to the substrate *I* in the presence of potassium fluoride. The dimerisation can be induced by relatively low concentrations of fluoride ions

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(Fig. 1). Methyl 2,3,3,3-tetrafluoropropanoate (*IV*) was found to be the side-product of dimerisation in solvents. Ratio of the diastereoisomers *IIIa* and *IIIb* depended predominantly on the solvent and on the reaction time. In acetonitrile, nitrobenzene or diethylene glycol dimethyl ether, the isomeric composition of the product *III* was independent of the solvent, reaction time and temperature (40–80°C). On the contrary, in dimethyl sulfoxide or dimethylformamide the *trans*-isomer *IIIb* highly predominated at the beginning but gradually the amount of both isomers neared to the same value. The presence of excess of potassium fluoride in the reaction mixture was essential. These facts led to the conclusion that in the mentioned solvents a subsequent *trans-cis* isomerisation [19] takes place.

TABLE I

Dimerisation of Methyl Trifluoropropenoate (*I*) (For reaction conditions see Experimental)

Solvent	Conversion %	Dimer yield %	Dimer *IIIa* % rel.	Dimer *IIIb* % rel.	*IV* yield[a] %
Acetonitrile	85	91	11	89	8
Tert-butyl alcohol	17	—	33	67	50
Diethylene glycol dimethyl ether	78	—	15	85	9
Dimethylformamide	91	—	43	57	15
Dimethyl sulfoxide	94	78	38	62	14
Nitrobenzene	100	86	12	88	5

[a] Approximate values found by gas–liquid chromatography without calibration.

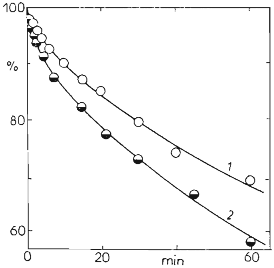
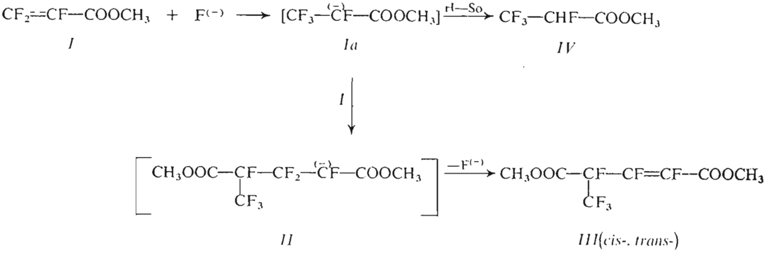


FIG. 1

Decrease of Methyl Trifluoroacrylate (*I*) in the Dimerisation Reaction (25°C, potassium fluoride concentration about $2 . 10^{-4}$ mol l^{-1})

Curve *1* concentration of *I* 0·14 mol l^{-1}, curve *2* concentration of *I* 0·27 mol l^{-1}.

The dimerisation mechanism has been discussed many times[1,2,6,12,13]. As far as we know, questions concerning the formation of configurational isomers of the dimers have not been as yet studied. We tried to prove that the suggested reaction mechanism (Scheme 1) involves the main steps of dimerisation of methyl trifluoropropenoate. The first step consists in formation of the carbanion *Ia*. In comparison with perfluoroolefins, its formation is facilitated by the fact that the electron density at C_3 in the substrate *I* is substantially lowered[18] in the σ- as well as in the π-bonding system. It is much lower even than in fluorinated ethylenes[20,21], *e.g.* in chlorotrifluoroethylene which also undergoes dimerisation[22]. Judging from the electron density which serves as a qualitative quantum chemical criterion of reactivity, particularly for nucleophilic reactions[23], the reaction of the substrate *I* with fluoride ion will be substantially easier than in the case of fluoroethylenes.



$$CF_2{=}CF{-}COOCH_3 + F^{(-)} \longrightarrow [CF_3{-}\overset{(-)}{C}F{-}COOCH_3] \xrightarrow{H-So} CF_3{-}CHF{-}COOCH_3$$

$$\left[CH_3OOC{-}\underset{CF_3}{CF}{-}CF_2{-}\overset{(-)}{C}F{-}COOCH_3\right] \xrightarrow{-F^{(-)}} CH_3OOC{-}\underset{CF_3}{CF}{-}CF{=}CF{-}COOCH_3$$

H—So = Solvent

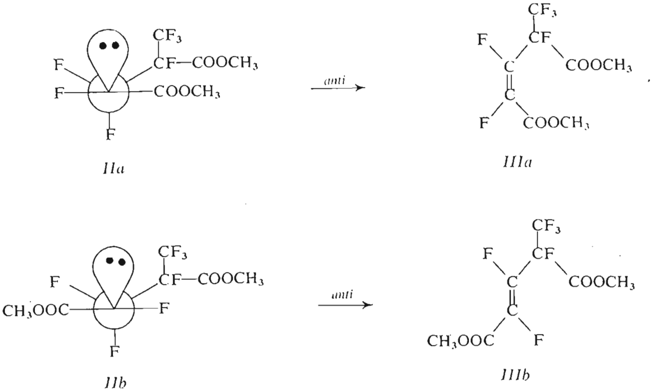
SCHEME 1

Stability of the intermediate *Ia* is affected by three substituents: F, CF_3 and $COOCH_3$. The stabilising effect of carbonyl group on carbanion formation is well known[24-27]. The remaining fluorine-containing substituents have a substantially different stabilizing effect, decreasing in the order[28] $CF_3 > Br > Cl > I > C_6H_5 > F > OCH_3$. This and other data[29,30] show that fluorine has a destabilizing effect in carbanions. However, we assume on the basis of the available evidence[24-30] that in the carbanion *Ia* the stabilizing effect of the groups $COOCH_3$ and CF_3 highly prevails over the reverse effect of the fluorine atom, ensuring thus a favourable enthalpy value for the reaction $I \rightarrow Ia$.

No values have been hitherto derived for the estimation of the spatial structure of fluorinated carbanions which would at the same time include non-fluorinated substituents, particularly those with a pronounced conjugation effect. The overall effect of such substituents on the carbanion geometry is not always evident, as shown by the published data: *e.g.* pyramidal structure was derived for[29] $(CF_3)_2CF^{(-)}$ (ref.[29]), $(CF_3)_2(C_6H_5)C^{(-)}$ (ref.[28]) and $C_6H_5CF_2^{(-)}$ (ref.[31-33]) whereas the carbanion $(CF_3)_3C^{(-)}$ is obviously planar[28,34]. We assume that in the carbanion *Ia* the $COOCH_3$ group will play a dominant role, tending[24-27] to create a planar or nearly planar pπ-conjugated carbanion. The fluorine atom in combination with a group having a $-K(-M)$ effect supports also the planar geometry[34,35] and simultaneously enhances the nucleophilicity[35] of the carbanion as far as reactivity is concerned.

On the other hand, we can consider the carbanion *Ia* as an E_1cB dehydrofluorination intermediate of the compound *IV*. In similar cases a carbanion, containing a CF_3 group, was so stable that isotopic exchange of hydrogen took place instead of elimination[36-38]. The carbanion *Ia* contains one stabilizing group more. Since the derivative *IV* was formed from *I* in all solvents employed (Table I) we assume that it represents a necessary side-product of the dimerisation in solvents, containing C—H bonds of sufficient acidity. We found that when the concentration of the propenoate *I* and fluoride in dimethyl sulfoxide was decreased by a factor of three, the amount of the product *IV* rose from 18% to about 50% relative to the dimer *III*.

Transformation of the intermediate *II* to the dimer *III* is irreversible[19] and very fast, faster than the reaction with solvent, because, contrary to the carbanion *Ia*, the carbanion *II* does not afford the hydrofluoro derivative of the type *IV*. This transformation represents the second step of an E_1cB type elimination reac-

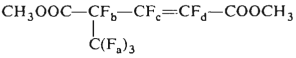


SCHEME 2

tion[36,37,39–41] in which the rate of the carbanion transformation is the same as the diffusion rate[39]. It follows from the result of this elimination reaction that in a very short time interval, *i.e.* faster than in diffusion controlled processes, the carbanion *II* occupies a conformation, leading to the transition state (Scheme 2). On the basis of the factors, mentioned above in the connection with the intermediate *Ia*, we assume that the anion *II* is planar.

The preferential formation of the *trans*-dimer *IIIb* suggests the factors operating in the transition state (Scheme 2). Conformations *IIa* and *IIb* depict the geometry of anions, favourable[36,3739–41] for the *anti*-elimination. Quantum chemical calculations of the interaction between carbanion electron pair and the fluorine atom on the neighbouring carbon by five semiempirical methods[42] show that conformation with torsion angle 180° is more advantageous than those with an angle 0° or 90°. If the fluoride ion is eliminated from the anion *II* by an *anti*-mechanism, the conformation *IIa* involves substantially greater interactions between bulky groups than the conformation *IIb*. These determine the preferential formation of the *trans*-dimer *IIIb*. The elimination of fluoride ion from the intermediate *II* is then a kinetically controlled reaction[43–45].

Structure of the compounds *IIIa*, *IIIb* and *IV* was determined by elemental analyses, NMR (Table II), mass and IR spectra. The isomers *IIIa* and *IIIb* were identified using chemical shifts and coupling constants in the ^{19}F-NMR model *V*.



$$CH_3OOC-\underset{\displaystyle C(F_a)_3}{\underset{|}{C}F_b}-CF_c{=}CF_d-COOCH_3$$

V

Table II

NMR Spectra of Compounds *IIIa*, *IIIb* and *IV*

Chemical shifts in ppm (number of protons or fluorine atoms); s singlet, d doublet, q quartet, m multiplet; coupling constants *J* in Hz; chemical shifts in the ^{19}F-NMR spectra relative to CCl_3F

Compound	Spectrum	Signals
IIIa, *IIIb*	^{1}H	s (3) 3·94; s (3) 3·98; (OCH_3)
IIIa	^{19}F	dm (1) —163·9 (CF_d), dd (1) —139·5 (CF_c), $^3J_{F_cF_d}$ 28; dqd (1) —128·9 (CF_b), $^3J_{F_bF_c}$ 21, $^3J_{F_bF_d}$ 4; m (3) —75·5 ($C(F_a)_3$), $^3J_{F_aF_b}$ 8
IIIb	^{19}F	dm (1) —153·6 (CF_d), m (1) —145·1 (CF_c), $^3J_{F_cF_d}$ 140; m (1) —170·4 (CF_b), m (3) —75·6 ($C(F_a)_3$), $^3J_{F_aF_b}$ 22
IV	^{1}H	s (3), 4·03 (OCH_3); dq (1) 5·22 (CHF); $^2J_{HF}$ 46, $^3J_{HF}$ 6
	^{19}F	dq (1) —205·7 (CHF), $^3J_{FF}$ 14; dd (3) —76·8 (CF_3)

EXPERIMENTAL

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 cm 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: Methyl trifluoropropenoate was prepared according to ref.[14–16]. Potassium fluoride (Lachema) was dried for 8 h at 120°C and 1·33 Pa; all manipulations with this compound were carried out in a dry atmosphere. The solvents used were purified and dried according to ref.[43,44].

Dimerisation of Methyl Trifluoropropenoate

A) *Preparative reaction.* A mixture of the monomer *I* (9 g; 64·2 mmol), potassium fluoride (1·5 g; 26 mmol) and acetonitrile (80 ml) was refluxed for 3 h, then diluted with 1,1,2-trichlorotrifluoroethane (30 ml), washed with water and dried over anhydrous magnesium sulfate. The low-boiling portion was distilled off under atmospheric pressure and the product *III* was collected, b.p. 98—100°C/2·7 kPa (20 Torr); preparative yield 6·48 g (72%), yield with complete conversion 86%, purity 98%. The product consisted of *IIIa* and *IIIb* (11 : 89) according to gas–liquid chromatography (15% poly(butanediol succinate), 120 cm column, 170°C, *IIIb* was eluted before *IIIa*). Reaction with the same amount of reactants in nitrobenzene (80 ml) after 7 h at 50°C gave 85% conversion and 90% yield of *III* (*IIIa* : *IIIb* = 13 : 87). The isomers *IIIa* and *IIIb* were isolated by preparative gas–liquid chromatography (*vide supra*). IR spectra (tetrachloromethane), cm^{-1}: *IIIa*: 1 035 m, 1 085 s, 1 123 m, 1 172 m, 1 179 m, 1 195 m, 1 208 s, 1 223 s, 1 248 m, 1 285 m, 1 307 s, 1 350 s, 1 435 m, 1 750 m ν(C=C), 1 769 vs and 1 796 m ν(C=O); *IIIb*: 1 037 m, 1 130 m, 1 190 s, 1 212 s, 1 215 s, 1 220 s, 1 285 vs, 1 296 m, 1 442 m, 1 759 vs ν(C=C), 1 774 m, 1 787 s and 1 800 s ν(C=O). Mass spectra (principal ions; *m/e*, rel. intensity, %): *IIIa*: 280/1,2 (M$^+$), 250/7 $(C_6F_6O_4)^+$, 236/11 $(C_7H_6F_6O_2)^+$, 221/13 $(C_6H_3F_6O_2)^+$, 191/7 $(C_7H_5F_2O_4)^+$, 186/3·3 $(C_6F_6)^+$, 162/3·3 $(C_4F_6)^+$, 159/10 $(C_4H_3F_4O_2)^+$, 93/14 $(C_3F_3)^+$, 69/5 $(CF_3)^+$, *59/100* $(C_2H_3O_2)^+$. *IIIb*: 280/0·7 (M)$^+$, 250/11 $(C_6F_6O_4)^+$, 219/9 $(C_6H_4F_5O_4)^+$, 190/6·4 $(C_5H_3F_5O_2)^+$, 161/3·4 $(C_5H_6F_6)^+$, 158/8 $(C_4H_2F_4O_2)^+$, 136/4·5 $(C_5H_3F_3O)^+$, 93/13 $(C_3F_3)^+$, 69/4·3 $(CF_3)^+$, *59/100* $(C_2H_3O_2)^+$. For $C_8H_6F_6O_4$ (280·2) calculated: 34·40% C, 2·16% H, 40·60% F; found for *IIIa*: 34·54% C, 2·07% H, 40·54% F; found for *IIIb*: 34·32% C, 2·19% H, 41·13% F.

B) *Reaction in solvents* (Table I). A mixture of the ester *I* (1·4 g; 10 mmol), potassium fluoride (1 g; 17·2 mmol) and the appropriate solvent (25 ml) was stirred for 6 h at 60°C. For gas–liquid chromatography see *A*.

C) *Reaction kinetics.* The dimerisation was carried out in dimethyl sulfoxide (40 ml). The decrease in the monomer *I* concentration was followed by gas–liquid chromatography, the detector response for *I* being calibrated with benzene as internal standard (concentration 0·01 and 0·02 mol l^{-1}). For gas–liquid chromatography see *A*.

Methyl 2,3,3,3-Tetrafluoropropenoate (*IV*)

A mixture of potassium fluoride solution (about $2 \cdot 10^{-4}$ mol l^{-1}) in anhydrous dimethyl sulfoxide (120 ml) and the compound *I* (4·9 g; 35 mmol) was stirred at 25°C. The relative increase of the product *IV* in the reaction mixture was as follows (min/% rel): 30/20·6, 60/38·6, 120/51 (according to gas-liquid chromatography on 20% poly(ethyleneglycol) 6000, 240 cm column, programmed temperature 80—200°C). After distilling off a mixture of products *III* and *IV*, (80°C bath at 2·7 kPa), the derivative *IV* was isolated by preparative gas-liquid chromatography (15% poly(butanediol succinate), 120°C); yield 1·72 g (35·4%), 99% purity. IR spectrum (tetrachloromethane), cm^{-1}: 1018 m, 1147 s, 1152 vs, 1202 vs, 1228 s, 1258 s, 1280 s, 1300 m, 1323 m, 1348 m, 1368 m, 1434 m; 1770 s, 1790 vs (C=O). Mass spectrum (see *III*): 160/2·3 $(M)^+$, 129/20 $(C_3H_4F_3O_2)^+$, 82/15 $(C_3HF_3)^+$, 59/100 $(C_2H_3O_2)^+$. For $C_4H_4F_4O_2$ (160·1) calculated: 30·02% C, 2·52% H, 47·48% F; found: 30·29% C, 2·59% H, 47·96% F.

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

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