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HALOACRYLIC ACIDS

XX[*]. DIMERISATION OF TRIFLUOROACRYLATES. KINETICALLY

AND THERMODYNAMICALLY CONTROLLED REACTIONS

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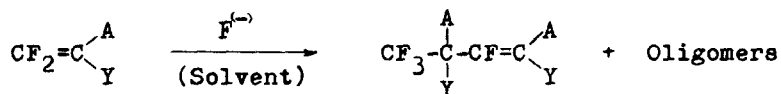Institute of Chemical Technology, 16628 Prague 6
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SUMMARY

    The potassium fluoride-catalysed dimerisation of methyl,
ethyl, isopropyl, butyl, and cyclohexyl trifluoroacrylate in
various solvents in the presence of solid potassium fluoride
was investigated and the main steps of the reaction mechanism
were proved. The preparative yields of the dimers amounted
to 74-87%. The dimerisation did not take place if potassium
fluoride was dissolved in the presence of dibenzo-18-crown-
-6-ether. From the high-boiling fractions two trimers of
methyl trifluoroacrylate were isolated. Dimerisation kinetics
in the heterogeneous system showed the reaction to be auto-
catalytic. The dimers are formed as a mixture of configu-
rational isomers with the trans isomer highly prevailing
under the kinetic control. The temperature dependence of the
kinetic distribution of the stereoisomeric dimers was measur-
ed, and compared with the thermodynamic distribution.

INTRODUCTION

Anionic dimerisation or oligomerisation induced by fluoride ions represents one of the characteristic reactions of perfluorinated olefins [1-4]. This reaction was performed with a large number of aliphatic and alicyclic substances and also compounds, containing perfluoroaromatic substituents [3].
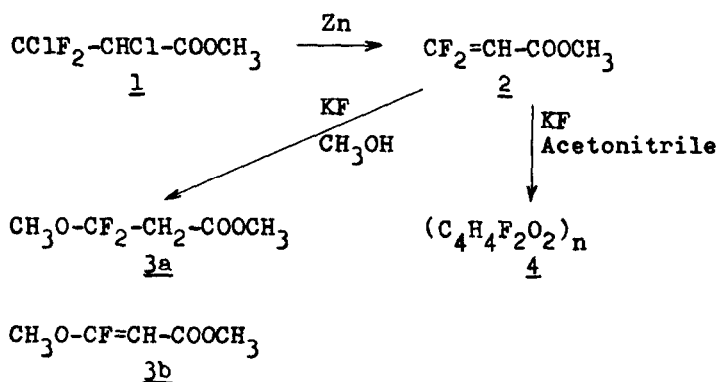
$$CF_2=C\overset{A}{\underset{Y}{\Big\langle}} \quad \xrightarrow[\text{(Solvent)}]{F^{(-)}} \quad CF_3-\overset{A}{\underset{Y}{\overset{|}{C}}}-CF=C\overset{A}{\underset{Y}{\Big\langle}} \quad + \quad \text{Oligomers}$$

$$A = F \ , \ CF_3 \ , \ \text{perfluoroalkyl}$$
$$Y = F \ , \ CF_3 \ , \ \text{perfluoroalkyl, perfluoroaryl,}$$
$$\quad COOR \ , \ CN$$

Also the dimerisation of some derivatives of perfluoro-methacrylic and trifluoroacrylic acids [5-7] follows the general scheme; the dimerisation of the latter is so fast that it is even difficult to keep these substances in the monomeric form. A more complicated course is characteristic for dimerisations or oligomerisations of olefins with chlorine bonded to the double bond, such as chlorotrifluoroethene [8] and methyl 2-chloro-3,3-difluoroacrylate [9]. These complications are probably caused [9] by a transfer of the chlorine cation to intermediate carbanions. In connection with the study of the dimerisation we developed a test for the reactivity of halogenated acrylates, consisting in addition of methanol to the substrate in the presence of anhydrous potassium fluoride. If the addition took place, a dimerisation reaction of the acrylate in question is to be expected.
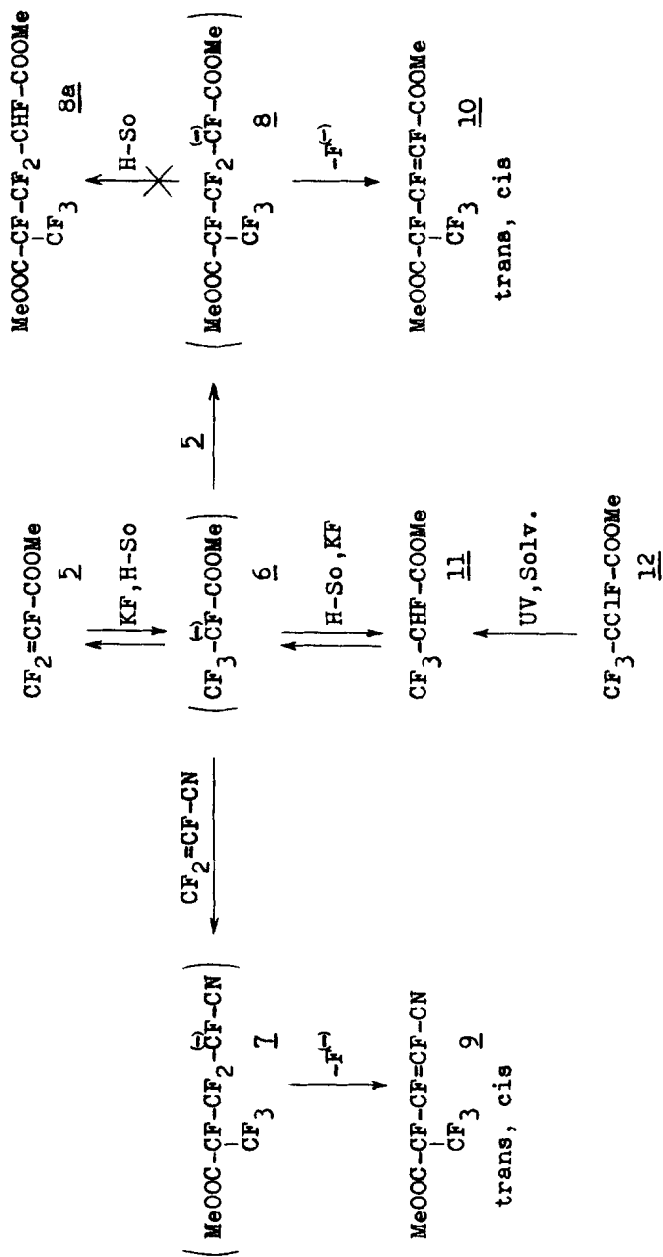
RESULTS AND DISCUSSION

As far as we know, no dimerisation or oligomerisation of a fluorinated olefin, containing a hydrogen atom in the double bond, has been described. As a model substance of such olefin we chose methyl 3,3-difluoroacrylate (2). Contrary to the previous syntheses [10-14], this compound was prepared by dehalogenation of methyl 2,3-dichloro-3,3-difluoropropanoate

(1) which was obtained by a photochemical reduction [15] of
methyl 2,3,3-trichlorodifluoropropanoate. The fluoroacrylate
2 added methanol under catalysis by potassium fluoride and
yielded methyl 3,3-difluoro-3-methoxypropanoate (3a) as the
main product (the unsaturated ether 3b was isolated as a side-
-product). The above-mentioned reactivity test was thus
positive, but when the dimerisation reaction was attempted,
instead of the dimer only a high-boiling substance was
obtained, which was probably an oligomer of the monomer 2,
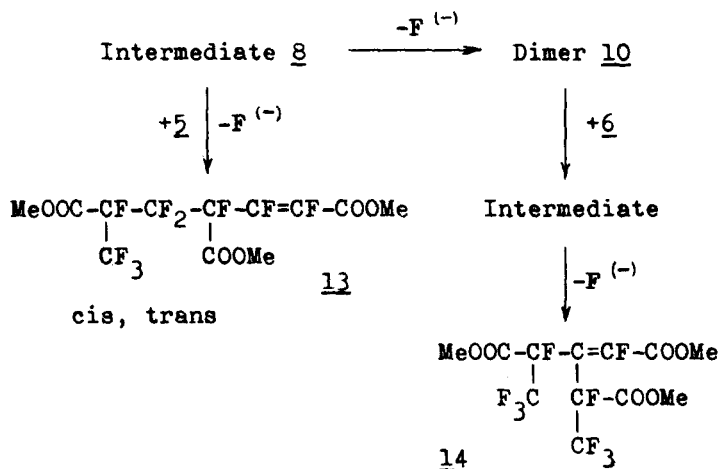as shown by its elemental analysis.

$$CClF_2-CHCl-COOCH_3 \xrightarrow{\;Zn\;} CF_2=CH-COOCH_3$$

$$\underline{1} \qquad\qquad\qquad \underline{2}$$

$$\xrightarrow[CH_3OH]{KF}$$

$$\Big| \begin{matrix} KF \\ Acetonitrile \end{matrix}$$

$$CH_3O-CF_2-CH_2-COOCH_3 \qquad (C_4H_4F_2O_2)_n$$

$$\underline{3a} \qquad\qquad\qquad \underline{4}$$

$$CH_3O-CF=CH-COOCH_3$$

$$\underline{3b}$$

The reaction pathway of the dimerisation of methyl
trifluoroacrylate in solvents (Scheme 1) includes two inter-
mediate carbanions, 6 and 8. The hydrofluoro derivative of the
starting compound, i.e. methyl 2,3,3,3-tetrafluoropropanoate
(11) is the side-product. The existence of the carbanion 6
was proved by its trapping with trifluoroacrylonitrile [16].
After spontaneous transformation of the intermediate carb-
anion 7 the resultant adduct was identified as methyl
4-cyanoperfluoro-2-methyl-3-butenoate (9). Since we were not
able to prove in the same way the intermediary carbanion 8
or its conjugated acid 8a, we suppose this species is of
a very short life. We assume, however, that the existence of
the intermediate 8 is evidenced by the steric effect, operating
in the transformation of the carbanion 8 (or 7) to the product
10 (or 9) affecting thus the distribution [17] of the cis and
trans isomers in the kinetic mixture.

$CF_2=CF-COOMe$ **2**

$CF_2=CF-CN$

$\left(CF_3-\overset{(-)}{CF}-COOMe \right)$ **6**

$CF_3-CHF-COOMe$ **11**

$CF_3-CClF-COOMe$ **12**

$\left(MeOOC-CF-CF_2-\overset{(-)}{CF}-CN \right)$ **7**
$\qquad\quad |$
$\qquad\quad CF_3$

$MeOOC-CF-CF=CF-CN$ **9**
$\qquad\quad |$
$\qquad\quad CF_3$
trans, cis

$MeOOC-CF-CF_2-CHF-COOMe$ **8a**
$\qquad\quad |$
$\qquad\quad CF_3$

$\left(MeOOC-CF-CF_2-\overset{(-)}{CF}-COOMe \right)$ **8**
$\qquad\quad |$
$\qquad\quad CF_3$

$MeOOC-CF-CF=CF-COOMe$ **10**
$\qquad\quad |$
$\qquad\quad CF_3$
trans, cis

KF, H-So

H-So, KF

UV, Solv.

H-So

−F$^{(-)}$

Me = Methyl
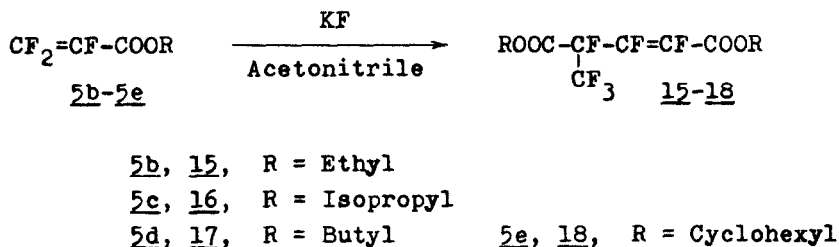H-So = Solvent

Scheme 1

Since the hydrofluoro derivative 11 and its functional
analogues are invariably formed in the dimerisation of tri-
fluoroacrylic acid derivatives in solutions [7,16], we tried
to show that the transformations $5 \rightleftarrows 6 \rightleftarrows 11$ were reversible
and that the substance of the type 11 was necessarily the
side-product of the dimerisation. The tetrafluoropropanoate
11 was prepared by a photochemical reduction [15] of methyl
2-chlorotetrafluoropropanoate (12). The starting substance 11
was then added to a suspension of potassium fluoride in
dimethyl sulfoxide or acetonitrile, and the dimer 10 was
identified as the reaction product. Thus, the reversibility
of the above-mentioned steps was proved.

$$\text{Intermediate } \underline{8} \xrightarrow{-F^{(-)}} \text{Dimer } \underline{10}$$

$$+\underline{5} \Bigg\downarrow -F^{(-)} \qquad\qquad \Bigg\downarrow +\underline{6}$$

$$\underset{\text{cis, trans}}{\underset{\underline{13}}{\overset{\text{MeOOC-CF-CF}_2\text{-CF-CF=CF-COOMe}}{\underset{\text{CF}_3 \qquad\quad \text{COOMe}}{|\qquad\qquad\quad|}}}} \qquad \text{Intermediate}$$

$$\Bigg\downarrow -F^{(-)}$$

$$\underline{14} \quad \underset{\overset{|}{\text{CF}_3}}{\underset{\overset{|}{\text{CF-COOMe}}}{\overset{\text{MeOOC-CF-C=CF-COOMe}}{\overset{|\quad|}{F_3C \quad CF}}}}$$

The dimerisation of trifluoroacrylate gave rise to minor
amounts of higher oligomers, which in acetonitrile did not
exceed 2-5 %, and in dimethyl sulfoxide amounted to about
10 %. A similar effect of these solvents was observed in the
oligomerisations of hexafluoropropene [18-23]. From the high-
boiling fractions resulting from dimerisation two substances
were isolated by column chromatography; their analyses
corresponded to trimers of methyl trifluoroacrylate (compounds
13 and 14). On the basis of their structure we conclude that
the trimer 13, i.e. dimethyl 4-methoxycarbonylperfluoro-6-
-methyl-2-heptenedioate, was formed by the addition

of the intermediate carbanion 8 to methyl trifluoro-
acrylate. In compounds 13 the cis and trans isomers were
identified by means of NMR spectra. The structure of the
product 14 suggested, on the other hand, that this compound
was formed by addition of the carbanion 6 to the dimer 10.

Analogously to the methyl ester, ethyl, isopropyl, butyl
and cyclohexyl trifluoroacrylate were dimerised to give the
dimers 15, 16, 17 and 18, respectively, in 74-87 % yields.

$$CF_2=CF-COOR \quad \xrightarrow[\text{Acetonitrile}]{\text{KF}} \quad ROOC-\underset{\underset{CF_3}{|}}{CF}-CF=CF-COOR$$

5b-5e   15-18

<div>
5b, 15,   R = Ethyl

5c, 16,   R = Isopropyl

5d, 17,   R = Butyl   5e, 18,   R = Cyclohexyl
</div>

The preparative dimerisations of the trifluoroacrylates
proceeded in the presence of undissolved potassium fluoride.
However, the dimerisation took place even when potassium
fluoride was completely dissolved in dimethyl sulfoxide [7]
at very low concentrations (ca. 10^{-5} mol L^{-1}). In order to
increase the fluoride concentration in the solution for
kinetic measurements, benzene was used as a solvent in
a mixture with dibenzo-18-crown-6-ether. Under these conditions,
however, no dimerisation took place. The reported [24-27]
favourable effect of crown-ethers on the rate of hexafluoro-
propene oligomerisation concerns probably reaction mixtures,
containing potassium fluoride. Therefore, we attemped to model
the dimerisation kinetically in a heterogeneous system; the
kinetic dependences are shown in Fig. 1. The curves show
a pronounced short induction period followed by an increase
in the reaction rate up to a conversion of ca. 70 %, which
indicates an autocatalysed reaction. It is not probable that
the autocatalytic effect should be attributed to the reaction
product, as is usually the case [28]. Also the solubility of
potassium fluoride will not be significantly influenced by
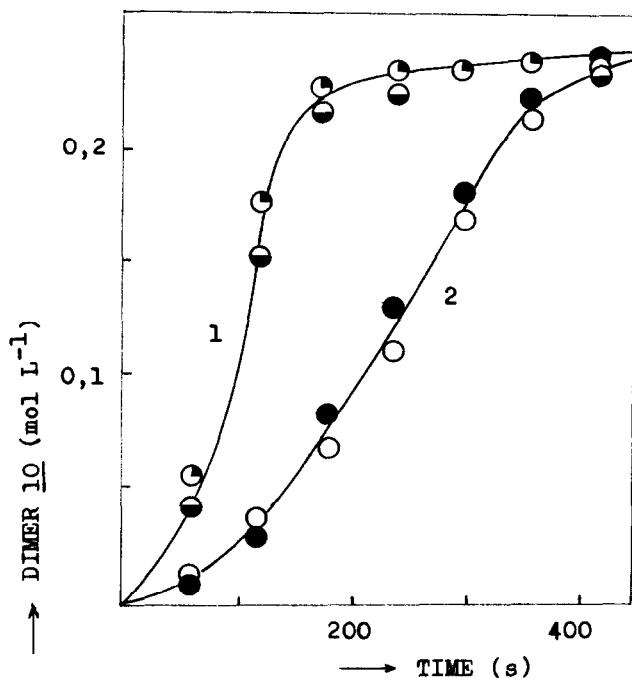the increasing dimer concentration. We are therefore of the

Fig. 1. Kinetics of the dimerisation of methyl trifluoro-
acrylate (5a). Curve 1: 11.1 ± 0.1°C; curve 2: 1.3 ± 0.1°C .
Initial concentration of the compound 5a (mol/L): ◐ 0.469 ,
◓ 0.479 , ○ 0.475 , ● 0.485 .

opinion that the autocatalytic effect is due to a change in
the surface structure of potassium fluoride during the re-
action. We assume that the dimerisation proceeds both in the
solution and on the catalyst surface or in its close vicinity.
During the reaction the fluoride ions can be set free from
the crystal lattice and the intermediate carbanions stabilised
on the catalyst surface. This hypothesis is supported to
a certain degree by the published results [29]. Since the
reaction system was rather complicated and the experimental
results depended on the quality of potassium fluoride, the
obtained results were not evaluated mathematically.

The obtained dimers 10, 15-17, are mixtures of
configurational isomers. As has been found [7,17], the amount
of the individual dimers depends on the solvent used and on
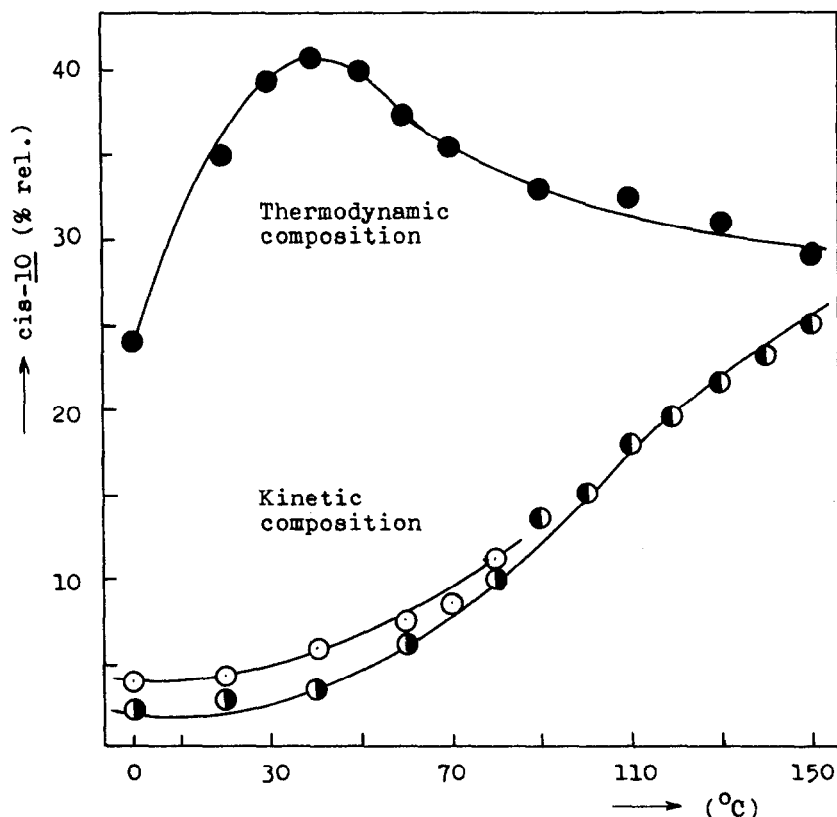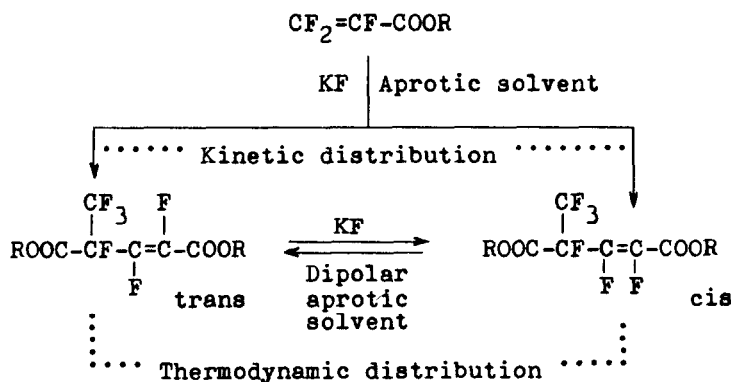the reaction temperature. In some dipolar aprotic solvents,

Fig. 2. Temperature dependence of the content of cis-dimer
10 in reaction mixture. Thermodynamic composition in dimethyl
sulfoxide. Kinetic composition:○ Dimerisation of methyl tri-
fluoroacrylate (5a) in acetonitrile; ◑dimerisation of iso-
propyl trifluoroacrylate (5c) in acetonitrile; ◐dimerisation
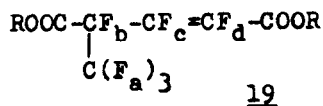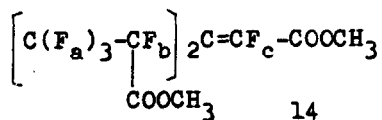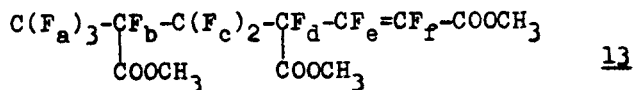of the compound 5c in nitrobenzene.

that are electron-pair donors, such as dimethyl sulfoxide,
dimethyl formamide, tetrahydrothiophene-1,1-dioxide and hexa-
methylphosphoric triamide (but not nitrobenzene), the resultant
configurational isomers are at equilibrium, their distribution
being thus thermodynamically controlled. The temperature
dependence of the equilibrium composition exhibits an unusual
course; since it has been already reported in our earlier
communication [17] for a series of dimers [30], its shape is
shown in Fig. 2 for one solvent.

When the dimerisation is not followed by isomerisation, the product exhibits a kinetic distribution of isomers, with a trans isomer highly predominating at room temperature. The kinetically and thermodynamically controlled distribution is shown on Scheme 2. The amount of the cis isomer slightly increases with increasing temperature (Fig. 2). From the quantitative data in Fig. 2 it follows out that the ratio of the stereoisomers depends only little on the ligand in the ester group. With increasing temperature the kinetic products composition approaches the thermodynamic composition. The results obtained show that in the dimerisation of trifluoroacrylates the kind of control depends on the solvent used.

$$CF_2=CF-COOR$$

KF │ Aprotic solvent

$\downarrow$ ······ Kinetic distribution ········ │

$$CF_3 \quad F \qquad\qquad\qquad\qquad CF_3$$
$$ROOC-CF-C=C-COOR \quad \xrightleftharpoons{KF} \quad ROOC-CF-C=C-COOR$$
$$\underset{F \quad trans}{|} \qquad \text{Dipolar} \qquad\qquad \underset{F\ F \quad cis}{|}$$
aprotic
solvent

⋮ ···· Thermodynamic distribution ·····⋮

Scheme 2

Structures of the newly prepared compounds 3a, 3b, 13-18 were determined by means of elemental analyses, IR and NMR spectra. The individual signals in the ^{19}F-NMR spectra are designated according to models 13, 14 and 19.

$$C(F_a)_3-CF_b-C(F_c)_2-CF_d-CF_e=CF_f-COOCH_3$$
$$\underset{COOCH_3}{|} \qquad\qquad \underset{COOCH_3}{|}$$

13

$$\left[C(F_a)_3-CF_b\right]_2 C=CF_c-COOCH_3 \qquad ROOC-CF_b-CF_c=CF_d-COOR$$
$$\underset{COOCH_3}{|} \qquad\qquad\qquad\qquad \underset{C(F_a)_3}{|}$$

14   19

EXPERIMENTAL

Apparatus

Gas chromatography
Chromatographic analyses were performed on a Chrom 41 (Laboratorní přístroje, Prague) instrument (FID, integrator with printer, column diameter 0.3 cm, carrier gas nitrogen, support Chromaton N-AW-DMCS, Lachema, Brno). Preparative gas chromatography was performed on a modified Chrom 2 instrument (FID with by-pass, column diameter 1 cm, length 500 cm).

Isothermal tempering
Kinetic and isothermal measurements were carried out using an U 10 (MLW Medingen) ultrathermostat.

NMR spectrometry
The NMR spectra were taken in deuteriochloroform on Varian XL-100/15 (Palo Alto) and Tesla BS 567 (Brno) instruments.

IR spectroscopy
The IR spectra were measured on a Perkin-Elmer 325 (Bodenseewerk) instrument.

Chemicals used

1,1,3-Trichlorotrifluoroethane (Ledon 113; Spolek pro chemickou a hutní výrobu, Ústí n. Labem). Ethyl trifluoro-acrylate (5b), isopropyl trifluoroacrylate (5c), butyl tri-fluoroacrylate (5d) and cyclohexyl trifluoroacrylate (5e) were prepared according to [31]. Methyl 2,3,3,3-tetrafluoro-propanoate (11) and methyl 2,3-dichloro-3,3-difluoropropano-ate (1) were synthesised according to [15,31,32]. Potassium fluoride was dried for 8 h at 160°C and 1.33 Pa, and handled in dry atmosphere only. The solvents were dried according to [16].

Methyl 3,3-difluoroacrylate (2)

To a mixture of zinc (83.7 g; 1.29 mol), activated with glacial acetic acid (3 ml), and diethylene glycol dimethyl ether (160 ml), methyl 2,3-dichloro-3,3-difluoropropanoate (100 g; 0.519 mol) was added dropwise at 160°C, and the crude product was collected continuously at 80-95°C. Rectification yielded 41.2 g (0.339 mol) of product 2, yield 65.3%, b.p. 80-82.5°C, 96% purity (GLC: 15% poly(propanediolsebacate), column length 250 cm, 80°C). For the IR and NMR spectra of the products see Tables 1 and 2, respectively. For $C_4H_4F_2O_2$ (122.1) calculated: 39.36% C, 3.30% H, 31.13% F; found: 39,62% C, 2,98% H, 31,68% F.

Methyl 3,3-difluoro-3-methoxypropanoate (3a)

To a stirred solution of potassium fluoride (0.2 g; 3 mmol) in methanol (6.3 g; 198 mmol) methyl 3,3-difluoro-acrylate (8 g; 65 mmol) was added at such a rate that the temperature of the reaction mixture did not exceed 30°C, and the mixture was stirred for 4 h. After dilution with Ledon 113 (15 ml), washing with water and drying with anhydrous magnesium sulphate the product 3a was obtained by distillation in the amount of 5.3 g (34 mmol), yield 52.3% , b.p. 54-58°C /3.3 kPa, purity 95%. As a high-boiling fraction methyl 3-fluoro-3-methoxypropenoate (3b) was obtained at 80-86°C /3.3 kPa, in the amount of 0.91 g (6.9 mmol), yield 10.4%, purity 91% (GLC: 15% poly(propanediol sebacate), column length 250 cm, 150 C). For the IR and NMR spectra of the products see Tables 1 and 2, respectively. For 3a, $C_5H_8F_2O_3$ (154.1) (154.1) calculated: 38.97% C, 5.23% H, 24.09% F; found: 38,54% C, 5.26% H, 24.12% F.
For 3b, $C_5H_7FO_3$ (134.1) calculated: 41.83% C, 5.26% H, 14.17% F; found: 41,70% C, 5.36% H, 14.12% F.

Oligomerisation of methyl 3,3-difluoropropenoate (2)

A mixture of the compound 2 (0.8 g; 6.6 mmol), potassium fluoride (0.4 g; 7 mmol) and acetonitrile (7 ml) was stirred at -10°C for 7 h. The reaction mixture was diluted with Ledon 113 (30 ml), washed with ice water, and dried over a molecular sieve (Potasit 3). After distilling off the solvent 0.5 g of the high-boiling substance (4) was obtained by vaccuum distillation (0.5-1.3 Pa). For $(C_4H_4F_2O_2)_n$ calculated: 39.36% C, 3.30% H, 31.13% F; found: 40.06% C, 3.54% H, 32.10% F.

Reaction of methyl 2,3,3,3-tetrafluoropropanoate (11) with potassium fluoride

A mixture of potassium fluoride (1.2 g; 20.7 mmol), tetrafluoropropanoate 11 (0.6 g; 3.7 mmol) and solvent (5 ml; acetonitrile, dimethyl sulfoxide) was heated at 40°C for 40 h and analysed (GLC: poly(propanediol sebacate), 150°C). The conversion of propanoate 11 to dimer 10 was ca. 2% in acetonitrile, the content of configurational isomers cis/trans = 5/95 was in agreement with previous data [17]. The conversion in dimethyl sulfoxide was ca. 18%, the ratio of stereoisomers in the product 10 cis/trans = 41/59 was in agreement with previous data [17].

Dimerisation of methyl trifluoroacrylate (5a)

(a) Preparative reaction

To a mixture of acetonitrile (800 ml) and potassium fluoride (23.4 g; 0,417 mol) the acrylate 5a (350 g; 2,5 mol) was added under stirring at 50°C within 15 min. After stirring the mixture for 1 h the conversion was complete. The reaction mixture was diluted with Ledon 113 (700 ml), washed with water and dried over anhydrous magnesium sulphate. Rectification yielded 306 g (1.09 mol) of the dimer 10, b.p. 99-102°C/ 2 kPa, purity 99%, yield 87.4%, content of stereoisomers cis/trans = 6.2/93.8 .

(b) In the presence of dibenzo-18-crown-6-ether

To a solution of potassium fluoride (5 ml; concentration 6×10^{-5} mol L^{-1}) in a mixture of the crown-ether and aceto-nitrile (concentration 0.0215 mol L^{-1}) the acrylate 5a was added at 25 C and its decrease followed by gas chromatography (poly(propanediol sebacate), 160°C). Even after a 1-hour reaction no formation of the dimer 10 was observed. After addition of solid potassium fluoride (0.0241 g; 0.48 mol) the reaction with complete conversion took place within 2 min. The ratio of stereoisomers was cis/trans = 5/95.

(c) In a solution of potassium fluoride in acetonitrile and benzene

To a solution of potassium fluoride in acetonitrile (5 ml; concentration ca. 10^{-5} mol L^{-1}) the acrylate 5a was added at 25°C (0.2276 g; 1.62 mmol) and the reaction course was followed as described under b). Even after 2 h no reaction occurred; the addition of solid potassium fluoride (0.312 g; 0.54 mmol) brought about dimerisation with complete conversion within 2 min. The ratio of stereoisomers was cis/trans = 5/95.

The reaction in a solution of potassium fluoride in benzene (concentration ca. 10^{-6} mol L^{-1}) gave analogous results, after the addition of fluoride the conversion being ca. 10% within 1 h.

(d) In a solution of potassium fluoride in dimethyl sulfoxide

To a saturated solution of potassium fluoride in dimethyl sulfoxide (10 ml; concentration ca. 10^{-4}mol L^{-1}) the acrylate 5a (0.26 g; 1.8 mmol) was added at 25°C. After 1 h the con-version was ca. 80%. The ratio of configurational isomers cis/trans = 9.1/90.9 remained constant with increasing reaction time.

An analogous reaction at 10°C occurred within 2 h with the conversion of ca. 20%, the ratio of isomers cis/trans = 6.2/93.8 being almost unchanged.

(e) Isolation of trimers 13 and 14

Besides the dimer 10 (yield 37.4 g; 74.8%) the dimer-
isation of acrylate 5a in dimethyl sulfoxide yielded also
3.2 g of a fraction boiling at 90-100°C/0.13 kPa. A part of
this fraction (0.5 g) was separated by column chromatography
(silica gel, eluent chloroform/petroleum ether 1:1), and
0.265 g (0.63 mmol) of dimethyl 4-methoxycarbonyl-perfluoro-
-6-methyl-2-heptenedioate (13), 95% purity, and 0.105 g
(0.25 mmol) of dimethyl 3-(1-methoxycarbonyltetrafluoroethyl)-
-perfluoro-4-methyl-2-pentenedioate (14), 95% purity (GLC:
poly(propanediol sebacate), 200°C) were isolated.
For $C_{12}H_9F_9O_6$ (420.1) calculated: 34.4% C, 2.16% H, 40.6% F;
found for 13: 34.28% C, 2.46% H, 39.64% F; found for 14:
34.36% C, 2.24% H, 39.02% F.

Dimerisation of alkyl trifluoroacrylates 5b-5e

(a) General procedure

A mixture of potassium fluoride (2.5 g; 0.051 mol), tri-
fluoroacrylate (0.15 mol) and acetonitrile (50 ml) was
stirred at a given temperature, then diluted with Ledon 113
(100 ml),washed with water, dried over anhydrous magnesium
sulphate, and the products (GLC: poly(propanediol sebacate),
160-200°C) were isolated. For the IR and NMR spectra of
products 15-18 see Tables 1 and 2, respectively.

(b) Dimerisation of ethyl trifluoroacrylate (5b)

The reaction of acrylate 5b at 40°C after 30 min. yielded
diethyl perfluoro-4-methyl-2-pentenedioate (15), b.p. 79-84°C
/20 Pa, yield 17.1 g (0.0555 mol), i.e. 74%, purity 98%,
ratio of cis/trans = 5.4/94.6 .
For $C_{10}H_{14}F_6O_8$ (308.2) calculated: 38.98% C, 3.27% H, 36.99%
F; found: 39.04% C, 3.22% H, 36.69% F.

(c) Dimerisation of isopropyl trifluoroacrylate (5c)

The reaction of trifluoroacrylate 5c at 40°C after 30
min. yielded diisopropyl perfluoro-4-methyl-2-pentenedioate
(16), b.p. 83-89°C/20 Pa, yield 21 g (0.0625 mol), i.e.
83.6%, purity 96%, ratio of cis/trans = 3.9/96.1 .
For $C_{12}H_{14}F_6O_4$ (336.2) calculated: 42.85% C, 4.23% H, 33.89%
F; found: 43.14% C, 4,45% H, 34.37% F.

TABLE 1

ABSORPTION MAXIMA (cm^{-1}) IN THE INFRARED SPECTRA OF THE COMPOUNDS (2, 3a, 3b, 11, 15-18) IN TETRACHLOROMETHANE AND CARBON DISULFIDE

Compound	Absorption bands
2	1035 m, 1138 s, 1208 m, 1282 m, 1364 m, 1441 m, 1715 s, 1738 s, 1753 s, 2850 w, 2960 w, 3000 w
3a	1000 m, 1050 m, 1095 m, 1127 m, 1180 s, 1200 s, 1240 s, 1297 s, 1355 s, 1380 s, 1140 s, 1453 s, 1758 s, 2770 w, 2805 w, 2973 w, 3008 w
3b	910 m, 1073 s, 1153 s, 1196 m, 1250 s, 1308 s, 1370 s, 1440 m, 1452 s, 1668 s, 1719 s, 1742 s, 2863 w, 2910 w, 2964 m, 3000 w
11	876 m, 985 m, 1021 s, 1120 s, 1140 s, 1153 s, 1202 s, 1228 s, 1279 s, 1281 s, 1302 s, 1326 s, 1349 s, 1370 s, 1445 s, 1770 s, 1789 s, 2868 w, 2980 w
15	1025 s, 1035 s, 1078 m, 1129 m, 1192 s, 1203 s, 1220 s, 1259 s, 1304 s, 1358 m, 1382 m, 1692 w, 1750 s, 1768 s, 1780 s, 1792 s, 2878 w, 2910 w, 2945 w, 2995 m
16	1025 s, 1075 m, 1102 s, 1128 m, 1148 m, 1188 s, 1210 s, 1257 s, 1300 s, 1381 s, 1389 m, 1470 m, 1690 w, 1748 s, 1762 s, 1776 s, 1789 s, 2950 w, 3000 m
17	1027 m, 1078 m, 1128 m, 1200 s, 1220 s, 1255 s, 1295 s, 1370 m, 1378 m, 1402 m, 1468 m, 1689 w, 1750 s, 1765 s, 1792 s, 2900 m, 2950 m, 2990 s
18	1009 m, 1023 m, 1078 m, 1125 m, 1189 s, 1256 s, 1300 s, 1367 m, 1392 m, 1453 m, 1690 w, 1742 s, 1760 s, 1772 s, 1788 s, 2870 m, 2950 s

TABLE 2

NMR SPECTRA OF THE COMPOUNDS ($\underline{2}$, $\underline{3a}$, $\underline{3b}$, $\underline{11}$, $\underline{13}$-$\underline{18}$)

Compound	Spectrum[a]	Character of signals[b]
$\underline{2}$	A	s 3.96 (3), dd 4.99 (1), $^3J(H\text{-}F)$ 3, $^3J(H\text{-}F)$ 22
	B	dd -71.2 (1), dd -65.4 (1), $^2J(F\text{-}F)$ 16
$\underline{3a}$	A	s 3.62 (3), s 3.83 (3), t 4.54 (1), $^3J(H\text{-}F)$ 6
	B	d -83.5 (1), d -80.1 (1), $^2J(F\text{-}F)$ 139
$\underline{3b}$	A	(E)-isomer: s 3.78 (3), d 4.71 (1), $^3J(H\text{-}F)$ 8
		(Z)-isomer: s 3.65 (3), s 3.94 (3), d 4.47 (1), $^3J(H\text{-}F)$ 27
	B	(E)-isomer: d -71.2 ; (Z)-isomer: d -65.5 (1)
$\underline{11}$	A	s 3.98 (3), dq 5.10 (1), $^2J(H\text{-}F)$ 39, $^3J(H\text{-}F)$ 7
	B	dq -205.5 (1), q -77.2 (3), $^3J(F\text{-}F)$ 12
$\underline{13}$	A	s 3.90 (3), s 3.94 (6)
	B	cis-isomer: m -162 (1, F_d), q -102.7 (1, F_b), $^3J(F\text{-}F)$ 15; dm -100,5 (1, F_e), $^3J(F\text{-}F)$ 17; dm -89.6 (1, F_f), m -74.9 (3, F_a), $^3J(F\text{-}F)$ ca. 5; dm -60.1 (2, F_c)
		trans-isomer: m -162.2 (1, F_d), q -99.5 (1, F_b), $^3J(F\text{-}F)$ 20; dm -96.8 (1, F_f), $^3J(F\text{-}F)$ 140; dm -92.8 (1, F_e), m -74.9 (3, F_a), dd -56.4 (2, F_c), $^3J(F\text{-}F)$ ca. 5
$\underline{14}$	A	s 3.87 (3), s 3.94 (6)
	B	m -104.3 (2, F_b), s -94.7 (1, F_c), m -75.1 (6, F_e)

15 A t 1.31 (6), q 5.24 (2), ^3J(H-H) 6

    B cis-isomer: m -169.5 (F_b), dm -152.5 (F_d), dm -151.5 (F_c), dd -75.2 (F_a),
       $^3J(F_c-F_d)$ 15, $^4J(F_b-F_d)$ ± $^3J(F_b-F_c)$ ≅ 6, $^3J(F_a-F_b)$ ± 4, $^4J(F_a-F_c)$ ± 6;
       trans-isomer: m -169.5 (F_b), ddq -144.7 (F_d), ddq -143 (F_c), dd -75.2
       (F_a), $^3J(F_c-F_d)$ 135, $^3J(F_b-F_c)$ ± $^4J(F_b-F_d)$ ≅ 25, $^3J(F_a-F_b)$ 20

       Coupling constants for the compounds 16, 17 and 18 have similar values
       and therefore are not reported.

16 A d 1.37 (12), q 5.24 (2), ^3J(H-H) 6

    B cis-isomer: m -168.8 (1), dm -152.2 (1), dm -150.5 (1), dd -74.4 (3);
       trans-isomer: m -168.8 (1), ddq -145 (1), ddq -143.5 (1), dd -74.4 (3)

17 A t 0.95 (6), q 1.41 (4), q 1.68 (4), t 4.37 (4), ^3J(H-H) 6.5

    B cis-isomer: m -169.5 (1), dm -152.5 (1), dm -151.3 (1), dd -75 (3)
       trans-isomer: m -169.5 (1), ddq -144.9 (1), ddq -143.9 (1), dd -75 (3)

18 A m 1.52 (12), m 1.79 (8), d 5.02 (2)

    B cis-isomer: m -168.6 (1), dm -152.2 (1), dm -150.4 (1), dd -75 (3);
       trans-isomer: m -168.6 (1), ddq -145.2 (1), ddq -143.7 (1), dd -75 (3)

(d) Dimerisation of butyl trifluoroacrylate (5d)

The reaction of trifluoroacrylate 5d at 40°C after 0.5 h yielded dibutyl perfluoro-4-methyl-2-pentenedioate (17), b.p. 104-110°C/13 Pa, yield 23.5 g (0.0645 mol), i.e. 86.1%, purity 98%, ratio of isomers cis/trans = 4.5/95.5 . For $C_{14}H_{18}F_6O_4$ (364.3) calculated: 46.16% C, 4.98% H, 31.29% F; found: 54.53% C, 5.05% H, 32.25% F.

(e) Dimerisation of cyclohexyl trifluoroacrylate (5e)

The reaction of trifluoroacrylate 5e at 80°C after 4 h yielded dicyclohexyl perfluoro-4-methyl-2-pentenedioate (18), b.p. 140-150°C/1.3 Pa, yield 17 g (0.048 mol), i.e. 85% with 80% conversion, purity 98%, ratio of isomers cis/trans = 4.1/95.9 . For $C_{18}H_{22}F_6O_4$ (416.4) calculated: 51.94% C, 5.33% H, 27.38% F; found: 52.68% C, 5.31% H, 28,36% F.

Dimerisation kinetics

(a) Apparatus

The reactions were carried out in a 10 ml glass flask closed with a perforable septum. The flask was surrounded with a glass jacket joined to a thermostat. The temperature was measured after outlet of the tempering water from the flask, and the flask was shaken thoroughly to keep the entire catalyst in dispersion.

(b) Chemicals and solutions

Potassium fluoride: The pre-dried substance was dried at 170°C/13 Pa for 6 h, finaly powdered in a dry atmosphere, and the drying repeated. Methyl trifluoroacrylate (5a) was rectified with a mixture of zinc and diethylene glycol dimethyl ether. The solution of chlorobenzene in acetonitrile (0.2 mol L^{-1}), serving as internal standard, was prepared in a nitrogen atmosphere. The reaction mixture consisted of 0.2 g potassium fluoride, 5 ml chlorobenzene solution, and ca. 0.6g acrylate 5a batched after tempering the reactor with the solution.

(c) Analysis of samples

For the taking of samples the shaking was stopped for 5-6 s, the withdrawn sample (ca. 20 μl) was added to a mixture of water and Ledon 113, shaken and stored in dry ice. The content of dimer 10 was calculated from the chromatogram by means of a calibration graph.

Temperature dependence of the content of stereoisomers in the dimerisation of trifluoroacrylates 5a, 5c

To a mixture of potassium fluoride (0.1 g; 1.7 mmol) and acetonitrile or nitrobenzene (1 ml), stirred vigorously, the acrylate 5a or 5c (1.8 mmol) was added at a given temperature. After a 0.5 h reaction the content of stereoisomers in the dimers 10 or 17 was determined by gas chromatography (GLC: 15% silicone elastomer E 301, column length 370 cm, 160°C). Analysis of samples showed the content of isomers was confirmed to be constant in the range of 0.5-3 h. The temperature dependence of the content of the cis-isomer is shown in Fig. 2

Compounds 3a, 3b, 13, 14, 15, 16, and 17 were new.

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