REACTION OF CHLORODIFLUOROPROPENOATES WITH POTASSIUM FLUORIDE*

Jiří SVOBODA, Oldřich PALETA and Václav DĚDEK
Department of Organic Chemistry,
Prague Institute of Chemical Technology, 166 28 Prague 6

Received July 11th, 1980

Reaction of methyl 3-chlorodifluoropropenoate (*I*) with potassium fluoride afforded methyl trifluoropropenoate (*II*) which was dimerized to dimethyl perfluoro-4-methyl-2-pentenedioate (*III*). The reaction rate of *I* was not affected by the presence of the monomer *II*. Methyl 2-chlorodifluoropropenoate (*VII*) on treatment with potassium fluoride underwent dimerization and the unstable dimer *X* was transformed at -20°C into methyl 2-chloro-3,5,5-trifluoro-4-methoxycarbonyl-2,4-pentadienoate (*XIII*) and dimethyl 2-chloro-3-fluoro-4-trifluoromethyl-2-pentenedioate (*XIV*). These reactions involve a transfer of chlorine atom from the dimer *X* to the primarily formed 1-chloro-3,3,3-trifluoro-1-methoxycarbonylethanide (*VIIa*) which is transformed by this carbanion interconversion into methyl 2,2-dichlorotrifluoropropanoate (*XI*). The propenoate *VII* adds methanol in the presence of potassium fluoride whereas the propenoate *I* does not react under these conditions.

In connection with our investigations[1] on dimerization of methyl trifluoropropenoate (*II*) we studied the behaviour of chlorinated analogues of this monomer, *i.e.* methyl 3-chlorodifluoropropenoate (*I*) and methyl 2-chlorodifluoropropenoate (*VII*), under similar conditions. The dimerization of propenoate *II* was analogous to the dimerization of hexafluoropropene[2] and other perfluoroalkenes[3-5]. However, there are no data available on dimerization or oligomerization of chloropentafluoropropenes as models of compounds *I* and *VII*. Only reactions of perhalogenochlorofluoropropenes with fluoride ion were studied[6,7]: these are terminated by a proton transfer and lead to products of ionic addition of hydrogen fluoride. Thus, *e.g.*, in the reaction of 3-chloropentafluoropropene[6] or 1,3-dichlorotetrafluoropropene[6] with potassium fluoride in formamide, nucleophilic substitution of chlorine with fluorine is followed by addition of hydrogen fluoride. In the case of 2-chloropentafluoropropene[7] the substitution did not take place and the olefin afforded a product of hydrofluorination, however, with greater difficulty than hexafluoropropene. Of chlorofluoroalkenes, the only compound hitherto subjected to oligomerization[8] was chlorotrifluoroethene. The reaction was more difficult and had a more complicated mechanism than the oligomerization of tetrafluoroethene[3-5,9]. On the basis of these

---

* Part XV in the series Haloacrylic Acids; Part XIV: This Journal *45*, 3360 (1980).

facts we chose the conditions of reaction of the halogenopropenoates *I* and *VII*. Derivatives of 3-chlorodifluoropropenoic and 2-chlorodifluoropropenoic acids were already prepared[10-13]; we synthetized their methyl esters *I* and *VII* using the previously described procedures[14].

Relative reactivity of halogenopropenoates *I* and *VII* was estimated by the base-catalyzed addition of methanol. The addition to 2-chlorodifluoropropenoate *VII* afforded methyl 2-chloro-3,3-difluoro-3-methoxypropanoate (*XV*), potassium fluoride being sufficient as catalyst, similarly as in the case of addition[15] of methanol to methyl trifluoropropenoate (*II*). On the contrary, under these conditions the addition of methanol to 3-chlorodifluoropropenoate *I* did not take place. Under catalysis with sodium methoxide, the reaction was more complex and we were not able to isolate the adduct with methanol, the only obtained products being dimethyl fluoropropanedioate (*V*) and methyl 2-fluoro-3,3,3-trimethoxypropanoate (*VI*). Thus, 2-chloropropenoate *VII* proved to be more reactive than the 3-chloropropenoate *I*.

Reaction of methyl 3-chlorodifluoropropenoate (*I*) with potassium fluoride in acetonitrile afforded dimethyl perfluoro-4-methyl-2-pentenedioate (*III*) as a mixture of configurational isomers (*cis* : *trans* = 15 : 85). An identical product with the same ratio of stereoisomers was obtained[1] by dimerization of the trifluoropropenoate *II*. During the reaction, the mixture contained about 1–2% of trifluoropropenoate *II* relative to the compound *I*. The time dependence of decrease in the amount of propenoate *I* is given in Fig. 1 (curve *1*). It is seen that the presence of the trifluoropropenoate *II* does not affect the dimerization rate of the starting compound *I*. The dimerization of *II* is much faster, a complete conversion being achieved in 2 h (Fig. 1, curve 2); on the other hand, only 40% of propenoate *I* reacted at 80°C after 29 h. Replacement of acetonitrile with tetrahydrothiophene 1,1-dioxide did not accelerate the reaction. From these facts and from the previous dimerization studies[1] it follows that the chlorofluoropropenoate *I* reacts first with potassium fluoride

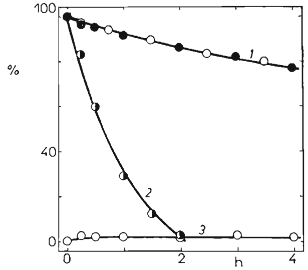
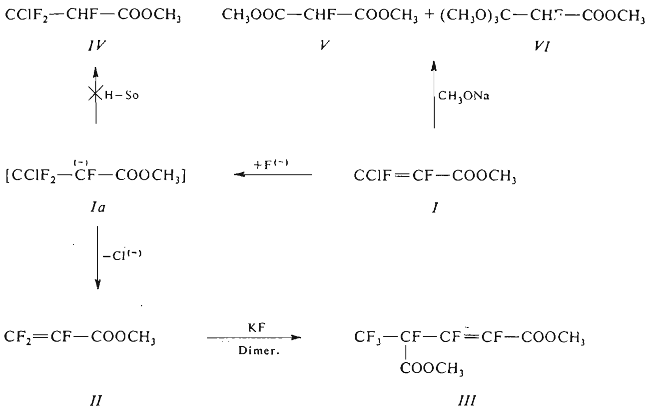


FIG. 1

Time Dependence of Decrease in Concentration of Propenoates *I* and *II* in the Dimerization Reaction

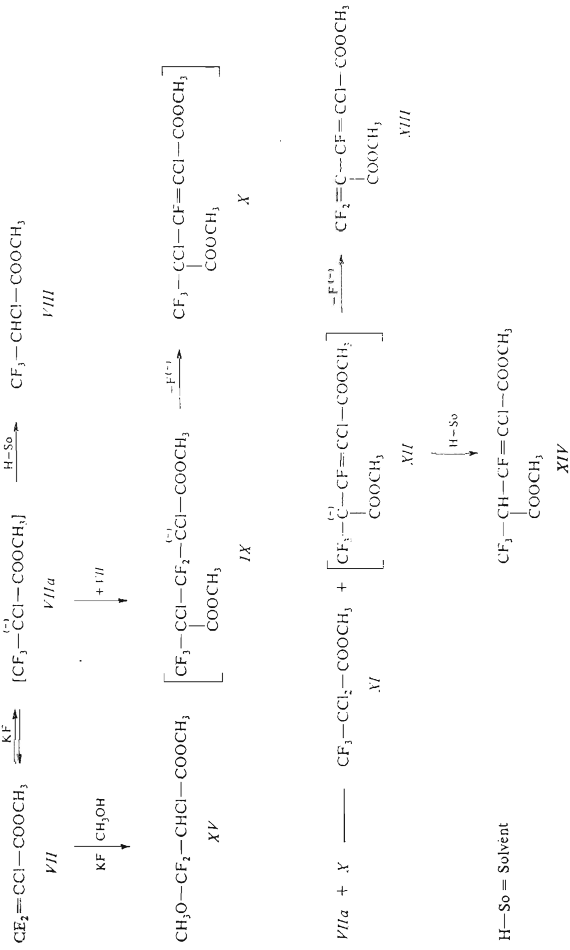
Curve *1* ○ propenoate *I*; curve *2* ◑ propenoate *II*; curve *1* ● equimolecular mixture of *I* and *II*; curve *3* ○ relative content of *II* in dimerization mixture of *I*, % are in relative values.



SCHEME 1

to give the perfluoropropenoate *II* (Scheme 1). This process represents a replacement of a vinylic chlorine by fluorine atom[16]. According to the present knowledge on the vinylic substitution of a halogen atom in fluorinated compounds[16] we assume that the reaction proceeds *via* carbanion *Ia* which after elimination of a chloride anion affords the perfluoropropenoate *II*. As calculated from the thermodynamic data[17], the transformation of *I* into *II* is extraordinarily advantageous, its ΔG being about $-168\,\text{kJ}\,\text{mol}^{-1}$ at 100°C which corresponds to an equilibrium constant $K \approx 10^{23}$. The reaction is therefore evidently irreversible. In the reaction mixture of *I* we did not find any propanoate *IV* which would arise by proton transfer from the solvent to the intermediary carbanion *Ia* as expected on the basis of previous observations[1,18,19]. However, the hydrofluoroderivative of the type *IV* did not arise if the carbanion underwent a fast subsequent reaction[1]. The dependence, depicted in Fig. 1, shows that transformation of *I* into the product *III* is much slower than dimerization of the propenoate *II* to dimer *III*. From these facts it follows that in the studied conversion of *I* into the product *III* formation of the intermediate *Ia* represents the slowest reaction step.

Unlike the isomeric propenoate *I*, 2-chloropropenoate *VII* reacted with potassium fluoride already at 20°C to give methyl 2,2-dichlorotrifluoropropanoate (*XI*) as the only isolable product, the rest being polymeric material. Performing the reaction at −20°C resulted in a substantial decrease in the amount of the polymeric products and from the reaction mixture we isolated, in addition to *XI*, methyl 2-chloro-


CF2=CCl—COOCH3
VII
KF
[CF3—C(-)Cl—COOCH3]
VIIa
H-So
CF3—CHCl—COOCH3
VIII
KF CH3OH
+VII
CH3O—CF2—CHCl—COOCH3
XV
CF3—CCl(COOCH3)—CF2—C(-)Cl—COOCH3
IX
-F(-)
CF3—CCl(COOCH3)—CF=CCl—COOCH3
X
VIIa + X
CF3—CCl2—COOCH3
XI
+
CF3—C(-)(COOCH3)—CF=CCl—COOCH3
XII
-F(-)
CF2=C(COOCH3)—CF=CCl—COOCH3
XIII
H-So
CF3—CH(COOCH3)—CF=CCl—COOCH3
XIV
H—So = Solvent

SCHEME 2

-3,3,3-trifluoropropanoate (*VIII*), methyl 2-chloro-3,5,5-trifluoro-4-methoxycarbonyl-2,4-pentadienoate (*XIII*) and dimethyl 2-chloro-3-fluoro-4-trifluoromethyl-2-pentenedioate (*XIV*); we did not find, however, the expected dimer of propenoate *VII*, *i.e.* the compound *X* (Scheme 2).

Carbon skeleton of products *XIII* and *XIV* corresponds to the dimer *X* but their structure indicates that the dimerization was followed by further reactions. The dichloropropanoate *XI* and the diene *XIII* are analogous to the compounds, isolated in the oligomerization of chlorotrifluoroethene[8] with cesium fluoride. We assume that addition of fluoride ion to the starting compound *VII* gives rise to the carbanion *VIIa* (Scheme 2) whose existence was proved[1,18] by isolation of compound *VIII*. This intermediate *VIIa* is transformed by the dimerization mechanism[1,18] into the

TABLE I

NMR Spectra of Compounds *I*, *V*—*VIII*, *XI*—*XV*

Chemical shifts in ppm (number of protons or fluorine atoms), coupling constants J in Hz; s singlet, d doublet, t triplet, m multiplet. The ^{19}F-NMR spectra relative to CCl_3F.

Compound	Spectrum	Character of signals
I	^{1}H	s(3) 3·92
	^{19}F	*cis*-isomer: d(1) −146·1, d(1) −81·8 $^{3}J_{FF} = 18·0$
		trans-isomer: d(1) −155·8, d(1) −96·3 $^{3}J_{FF} = 130·5$
V	^{1}H	s(3) 3·96, d(1) 5·32 $^{2}J_{HF} = 48·0$
	^{19}F	d(1) −199·6
VI	^{1}H	s(9) 3·41, s(3) 3·82, d(1) 5·01 $^{2}J_{HF} = 48·0$
	^{19}F	d(1) −198·5
VII	^{1}H	s(3) 3·98
	^{19}F	d(1) −68·2, d(1) −66·8 $^{2}J_{FF} = 16·0$
VIII	^{1}H	s(3) 3·96, m(1) 4·67
	^{19}F	d(3) −72·7 $^{3}J_{HF} = 6·0$
XI	^{1}H	s(3) 3·96
	^{19}F	s(3) −75·3
XIII	^{1}H	s(6) 3·88
	^{19}F	d(1) −73·5, d(1) −70·1 $^{4}J_{FF} = 7·0$, d(2) −63·0 $^{2}J_{FF} = 17·0$
XIV	^{1}H	s(6) 3·84, m(1), 5·12
	^{19}F	m(1) −95·0 a −87·2 $^{4}J_{FF} = 6·5$, d(3) −65·4
XV	^{1}H	s(3) 3·62, s(3) 3·83, t(1) 4·54 $^{3}J_{HF} = 6·0$
	^{19}F	d(1) −83·5, d(1) −80·1 $^{2}J_{FF} = 139·0$

dimer *X* which, unlike the perfluoro dimer *III*, is unstable. It reacts with the carbanion *VIIa* through transfer of a chlorine-cation-type intermediate, giving rise to the propanoate *XI* and carbanion *XII*. Analogous interconversions of carbanions were observed[8] in the mentioned oligomerization of chlorotrifluoroethene and similar mechanism has been suggested[20] for the formation of unsaturated esters from polychlorofluorobutanoates by action of potassium fluoride. The intermediate *XII* is stabilized by elimination of the fluoride ion under formation of the diene *XIII* or by transfer of proton from the solvent to give the product *XIV*. The isolation of the product *XIV* proves that the reaction proceeds *via* the carbanion *XII*. The low yield of the diene is caused by its propensity to further transformations connected with polymerization.

Structure of compounds *I–III*, *V–VIII*, *XI*, *XIII–XV* was determined by the NMR (Table I), IR and mass (compounds *XIII* and *XIV*) spectra and elemental analyses. The diastereoisomers of compounds *III*, *XII* and *XIV* were not separated and they were identified by chemical shifts and spin interactions in the NMR spectra.

EXPERIMENTAL

Temperature data are uncorrected. Gas–liquid chromatography was carried out on Chrom 3 and Chrom 41 instruments (Laboratorní přístroje, Prague); flame-ionization detector, column diameter 0·6 or 0·3 cm, integrator, support Chromaton N-AW-DMCS (Lachema, Brno). Infrared spectra were taken on a Perkin-Elmer 325 spectrometer (Bodenseewerk). NMR spectra were recorded on a Varian XL-100-15 (Palo Alto) instrument in deuteriochloroform; ^{19}F-NMR spectra were taken with CCl_3F as standard. Mass spectra were measured on a Gas-Chromatograph-Mass Spectrometer LKB 9000 (Stockholm); one-focus, 70 eV, chromatographic inlet poly(propanediol sebacate), carrier gas helium.

Methyl 3-chlorodifluoropropenoate (*I*) (*cis* : *trans* = 36 : 64) and methyl 2-chlorodifluoropropenoate (*VII*) were prepared according to the described[14] procedures. The solvents and potassium fluoride were purified and dried as described in ref.[19].

Reaction of Methyl 3-Chlorodifluoropropenoate with Potassium Fluoride

A) A mixture of the propenoate *I* (12·0 g; 0·077 mol), potassium fluoride (6·5 g; 0·112 mol) and acetonitrile (80 ml) was stirred at 80°C for 29 h, diluted with 1,1,2-trichlorotrifluoroethane (100 ml), washed with water and dried over anhydrous magnesium sulfate. Distillation afforded 1·6 g (5·7 mmol) of dimethyl perfluoro-4-methyl-2-pentenedioate (*III*), b.p. 98–100°C/2·7 kPa, purity 96%, *cis* : *trans* = 15 : 85 (according to gas–liquid chromatography on poly(butanediol succinate) at 175°C). Yield of *III* 89%, conversion of *I* 39·6%. For $C_8H_6F_6O_4$ (280·1) calculated: 34·40% C, 2·16% H, 40·60% F; found: 34·32% C, 2·19% H, 41·13% F.

B) The propenoate *I* in tetrahydrothiophene 1,1-dioxide (80 ml) afforded after 21 h at 100°C the dimer *III* (6·02 g; 21·4 mmol); yield 80%, conversion of *I* 62·7%, recovered 4·5 g (28·8 mmol) of the starting ester *I*.

C) A mixture of 1·2M solution (30 ml) of *I*, *II* or their equimolar mixture in acetonitrile, potassium fluoride (3·0 g; 52 mmol) and benzene (1·0 g; 12·8 mmol; internal standard) was stirred at 80°C and its composition was followed by gas–liquid chromatography (Carbowax 6000, 90°C). The time dependence of the content of *I* and *II* in the mixture is given in Fig. 1.

Dimerization of Methyl 2-Chlorodifluoropropenoate (*VII*)

A) *At* 20°C: A mixture of the ester *VII* (5·3 g; 34 mmol), potassium fluoride (2·1 g; 36 mmol) and 1,2-dimethoxyethane (25 ml) was stirred for 8 h, diluted with 1,1,2-trichlorotrifluoroethane (50 ml), washed with water and dried over anhydrous magnesium sulfate. Distillation afforded 3·5 g (49%) of methyl 2,2-dichloro-3,3,3-trifluoropropanoate (*XII*), b.p. 102—103°C. Its NMR spectrum is given in Table I; IR spectrum (tetrachloromethane, carbon disulfide), cm^{-1}: 712 m, 787 m, 885 s, 955 m, 1020 s, 1205 s, 1240 s, 1265 s, 1442 m, 1773 s, 2855 w, 2970 w, 3015 w. For $C_4H_3Cl_2F_3O_2$ (211·0) calculated: 22·67% C, 1·43% H, 33·65% Cl, 27·00% F; found: 23·18%C 1·61% H, 33·70% Cl, 27·86% F.

B) *At* —20°C: A mixture of the ester *VII* (10·5 g; 67 mmol), potassium fluoride (4·0 g; 69 mmol) and acetonitrile (50 ml) was stirred for 3 h, diluted with trichlorofluoromethane (100 ml), washed with ice-cold water and dried over anhydrous magnesium sulfate. Distillation afforded a fraction, boiling (2·1 g) at 30—33°C/4 kPa, consisting of the ester *XII* (90%) and methyl 2-chloro-3,3,3-trifluoropropanoate (*VIII*; 10%), and a fraction (3·3 g), boiling at 96—105°C/4 kPa, which contained *XIII* (71%) and *XIV* (29%) (according to gas-liquid chromatography on SE-301 at 160°C). The individual compounds were obtained by preparative gas-liquid chromatography on poly(propanediol sebacate) at 178°C. The NMR spectra of compounds *VIII*, *XIII* and *XIV* are given in Table I. IR spectra (tetrachloromethane or carbon disulfide), cm^{-1}: compound *XIII*: 1045 s, 1068 s, 1130 m, 1181 s, 1230 s, 1260 s, 1295 s, 1325 m, 1442 s, 1658 w, 1728 s, 1750 s, 1774 s, 2826 w, 2900 w, 2970 m, 3010 w; compound *XIV*: 1043 m, 1068 m, 1130 s, 1180 s, 1250 s, 1293 s, 1370 w, 1441 s, 1634 w, 1760 s, 1778 s, 2962 w, 2980 w, 3010 w. Mass spectra (*m*/*e*, rel. intensity, %): compound *XIII*: 260/0·6 and 258/2 M^+, 229/14 and 227/21 $(M-CH_3O)^+$, 173/5 and 171/16 $C_5H_3ClF_3O^+$, 142/4 and 140/10 $C_4ClF_3^+$, 121/17 $C_4H_3F_2O_2^+$, 105/8 $C_4H_3^+$, 93/7 $C_3F_3^+$, 90/7 $C_3F_2O^+$, 87/5 C_3ClO^+, 71/8 $C_3H_3O_2^+$, 59/100 $C_2H_3O_2^+$, 50/3 CF_2^+, 31/11 CF^+; compound *XIV*: 278/36 M^+, 258/2 $(M-HF)^+$, 218/6 $C_6H_3ClF_3O_2^+$, 206/10 $C_5H_3ClF_4O_2^+$, 177/8 and 175/15 $C_4H_3ClF_3O_2^+$, 161/6 and 159/16 $C_4ClF_4^+$, 140/4 $C_4H_3F_3O_2^+$, 125/11 $C_3F_3O_2^+$, 111/8 and 109/21 $C_3ClF_3^+$, 93/10 $C_3F_3^+$, 90/8 $C_3H_3FO_2^+$, 81/10 $C_2F_3^+$, 71/9 $C_3H_3O_2^+$, 69/17 CF_3^+, 59/100 $C_2H_3O_2^+$, 31/8 CF^+.

Addition of Methanol to Methyl 3-Chlorodifluoropropenoate (*I*)

A solution of sodium methoxide in methanol was added dropwise at 20°C to a solution of the propenoate *I* (4·5 g; 28·8 mmol) in methanol (10 ml) until complete conversion was achieved. The mixture was diluted with 1,1,2-trichlorotrifluoroethane (50 ml), washed with water and dried over anhydrous magnesium sulfate. Distillation afforded 2·3 g of a fraction boiling at 90—95°C/4 kPa, consisting of dimethyl fluoropropanedioate (*V*; 40%) and methyl 2-fluoro-3,3,3-trimethoxypropanoate (*VI*; 60%). For NMR spectra see Table I. Mass spectra (*m*/*e*, relative intensity, %): compound *V*: 150/2 M^+, 119/22 $(M-CH_3O)^+$, 91/28 $(M-C_2H_3O_2)^+$, 88/11 $C_3HFO_2^+$, 72/16 $C_3H_4O_2^+$, 71/12 $C_3H_3O_2^+$, 59/100 $C_2H_3O_2^+$, 32/18 CHF^+, 31/38 CH_3O^+; compound *VI*: 164/46 $(M-CH_3OH)^+$, 133/10 $C_5H_6FO_3^+$, 105/21 $C_4H_6FO_2^+$, 102/8 $C_4H_3FO_2^+$, 87/28 $C_4H_7O_2^+$, 74/25 $C_3H_3FO^+$, 71/18 C_3FO^+, 59/100 $C_2H_3O_2^+$, 44/14 C_2HF^+, 43/11 C_2F^+, 32/24 CHF^+, 31/86 CH_3O^+.

Addition of Methanol to Methyl 2-Chlorodifluoropropenoate (*VII*)

The propenoate *VII* (6·0 g; 38 mmol) was added dropwise during 4 h at 20°C to a stirred solution of potassium fluoride (0·2 g; 3 mmol) in methanol (6·3 g; 38 mmol). Distillation afforded 3·7 g (51·7%) of methyl 2-chloro-3,3-difluoro-3-methoxypropanoate (*XV*), b.p. 59—61°C/2 kPa; purity 97%. Gas-liquid chromatography was performed on poly(propanediol sebacate) at 150°C; for NMR spectrum see Table I. IR spectrum (tetrachloromethane, carbon disulfide), cm^{-1}: 1013 s, 1060 s, 1140 s, 1163 s, 1208 s, 1241 s, 1295 s, 1320 s, 1439 s, 1452 m, 1753 s, 2855 w, 2930 w, 2970 w, 3010 w. For $C_5H_7ClF_2O_3$ (188·6) calculated: 31·85% C, 3·74% H, 18·80% Cl, 30·23% F; found: 32·08% C, 3·78% H, 19·19% Cl, 29·49% F.

The elemental analyses were carried out in the Department of Organic Analysis (Dr L. Helešic, Head), spectral measurements were performed in the Laboratory of NMR *Spectroscopy (Dr P. Trška, Head), Absorption Spectroscopy (Dr A. Muck, Head) and Mass Spectrometry (Dr V. Kubelka, Head), of Prague Institute of Technology. We are indebted to all of them for kind help.*

REFERENCES

1. Paleta O., Havlů, V., Dědek V.: This Journal *45*, 415 (1980).
2. Dresdner R. D., Tlumac F. N., Young J. A.: J. Org. Chem. *30*, 3524 (1965).
3. Young J. A. in the book: *Fluorine Chemistry Reviews* (P. Tarrant, Ed.), Vol. 1, p. 359. Dekker, New York 1967.
4. Chambers R. D. in the book: *Fluorine in Organic Chemistry*, p. 167. Wiley, New York 1973.
5. Svoboda J.: Chem. Listy *74*, 469 (1980).
6. Miller W. T., Jr, Fried J. H., Goldwhite H.: J. Amer. Chem. Soc. *82*, 3091 (1960).
7. Fried J. H., Miller W. T., Jr: J. Amer. Chem. Soc. *81*, 2079 (1959).
8. Chambers R. D., Lindley A. A., Philpot P. D., Fielding H. C., Hutchinson J.: Isr. J. Chem. *17*, 150 (1978).
9. Graham D. P.: J. Org. Chem. *31*, 955 (1966).
10. Chaney D. W.: U. S. 2 456 768 (1948); Chem. Abstr. *43*, 4683 (1949).
11. Stoner G. G.: U.S. 2 761 875 (1956); Chem. Abstr. *51*, 3657 (1957).
12. Miller W. T.: U.S. 2 751 414 (1956); Chem. Abstr. *51*, 2849 (1957).
13. Ivanyk G. D., Politanskii S. F., Shevchuk V. U.: U.S.S.R. 455 951 (1975); Chem. Abstr. *82*, 124 825 (1975).
14. Paleta O., Pošta A., Novotná Z.: This Journal *33*, 2970 (1968).
15. Paleta O., Kohárek J.: This Journal *38*, 66 (1973).
16. Rappoport Z.: *Advances Physical Organic Chemistry*, Vol. 7 (V. Gold, Ed.), p. 31, 46, 50. Academic Press, London 1969.
17. Yoneda Y.: Bull. Chem. Soc. Jap. *52*, 1297 (1979).
18. Svoboda J., Paleta O., Dědek V.: This Journal *45*, 406 (1980).
19. Paleta O., Svoboda J., Havlů V., Dědek V.: This Journal *45*, 3360 (1980).
20. Battais A., Boutevin B., Pietrasanta Y.: J. Fluorine Chem. *14*, 467 (1979).

Translated by M. Tichý.