Journal of Fluorine Chemistry, *45* (1989) 331–348

Received: December 22, 1988; accepted: July 7, 1989

THE CHEMO-SELECTIVE REDUCTION OF FLUORINATED HALOGENOESTERS WITH SODIUM BOROHYDRIDE. FLUORINATED HALOGENOALKANOLS AND THEIR (METH)ACRYLATES

O. PALETA, A. DANDA, L. ŠTĚPÁN, J. KVÍČALA and V. DĚDEK

Department of Organic Chemistry, Prague Institute of Chemical Technology, 16628 Prague 6 (Czechoslovakia)

SUMMARY

Several chlorofluoroalkanols R_F-CH_2OH (R_F is CF_3-$CFCl$, CF_2Cl-CF_2, CF_2Cl-$CFCl$ and CF_2Cl) and their methacrylates or acrylates were synthesized. The corresponding polymeric methacrylates have properties of highly-sensitive electron-beam and X-ray resists for microlithography. The main step in the syntheses, which start from halogenoalkanes R_F-CCl_3 , is the chemo-selective reduction of halogenoesters with sodium borohydride, in which the C-Cl bonds in the acyl parts of the esters are not attacked. Relative rates of the reductions of esters R_F-$COOCH_3$ are influenced by the structure of halogenoalkyls R_F in the order CF_2Cl : CF_3-$CFCl$: CF_2Cl-$CFCl$ = 4.5 : : 3.5 : 1 . A remarkable reactivity decrease in the reduction rate in the structure possessing a Cl atom at the β-position in the acyl group is discussed.

INTRODUCTION

Fluorinated alkanols have become valuable intermediates in the preparation of the corresponding methacrylates and their polymers. Recently, these polymer substances have found application in microelectronics and optoelectronics. In microelectronics, the mentioned polymers are exploited as resists with a high sensitivity to electron beams and X-ray radiation

0022-1139/89/$3.50

[1-3]. Polymeric methacrylates of chlorofluoroalkanols 5a, 5b, 12 and 17, for e.g., whose syntheses are presented in this publication, exhibit advantageous properties as electron-beam resists for microlithography (Table 1) [4,5]. The presence of a chlorine atom in a resist molecule generally enhances the

TABLE 1
Electron-beam resist properties of some chlorofluoroalkyl methacrylates [5]

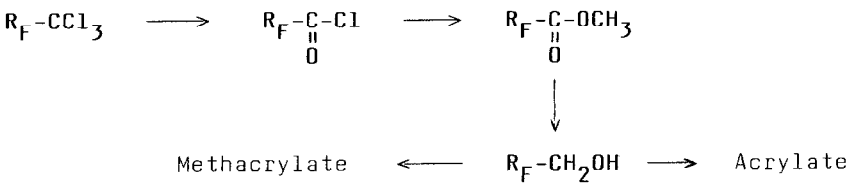
Monomer	Sensitivity 10^{-6} C cm^{-2}	Contrast γ
CF_3-CFCl-CH_2-O-MA[a] (5a)	5.1	3.3
5a + MMA[b]	6.1	2.5
5a + EPMA[c]	5.3	2.8
C_2ClF_4-CH_2-O-MA (5a + 5b)	5.4	3.4
CF_2Cl-CFCl-CH_2-O-MA (12)	7.3	2.9
CF_2Cl-CH_2-O-MA (17)	3.0	1.6
17 + MMA	10.1	1.3

[a] MA - Methacryloyl ;
[b] MMA - methyl methacrylate ;
[c] EPMA - (2,3-epoxypropyl)-2-methyl-2-propenoate .

resist sensitivity to some bands of roentgen radiation [6]. From this point of view, methacrylates of fluorinated halogenoalkanols appear to be prospective resists for X-ray microlithography. A recent publication [7] deals with the potential application of chlorofluoroalkyl methacrylates in optoelectronics.

The former one-step syntheses of halogenopropanols 4a, 4b and 11 [8,9] afforded these compounds in a mixture with other products and in relatively low yields with respect to potential application. We used halogenoalkanes containing a terminal CCl_3-group as starting compounds for the syntheses. These compounds are easily accessible from industrial products

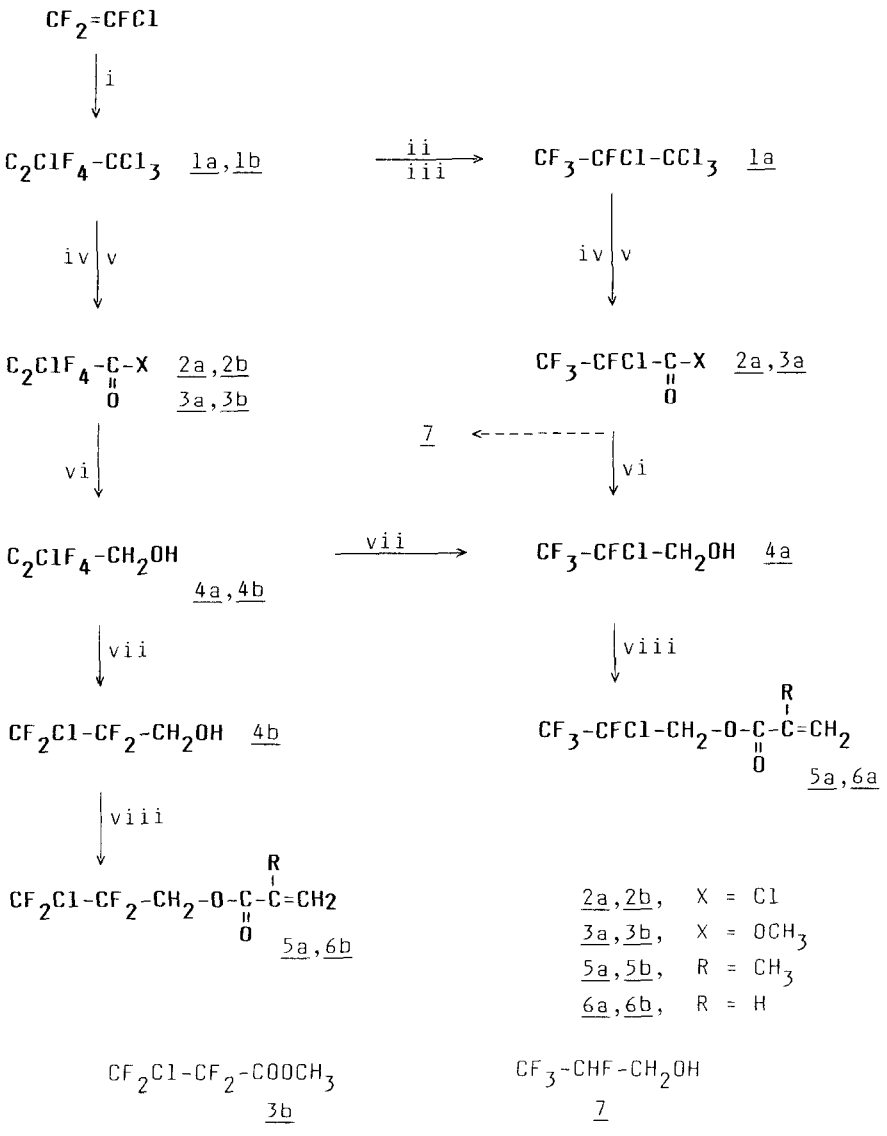
and their preparation was described formerly [10-13]. In the course of the synthetic route, the CCl_3-group in halogenoalkanes is stepwise converted to a hydroxymethyl group according to a general scheme:



The reduction of esters of fluorinated acids to the corresponding alkanols with complex hydrides, namely with lithium aluminium hydride, belongs to general preparative methods (e.g. reviews [14,15]). However, if other halogen atoms are present in an acyl group, then partial reductions can take place [16-18] in addition to the total reduction of the ester group. Therefore one of the aims of the present publication was to find convenient preparative conditions and a complex-hydride reducing agent not attacking halogen bonds. Sodium borohydride in a medium of diethyl ether proved to be the most suitable agent in all our cases.

RESULTS AND DISCUSSION

The synthesis of isomeric chlorotetrafluoropropanols 4a, 4b on the basis of chlorotrifluoroethylene and their transformation to methacrylates and acrylates is depicted in Scheme 1. The preparation of tetrachlorotetrafluoropropane 1 and the separation of isomers 1a, 1b can be easily performed on a larger scale [10,13]. The isomer content, both in the starting mixture and in the separated isomers 1a, 1b, can be determined with advantage by means of ^{19}F NMR spectra [19]. The oxygenative dechlorination in the CCl_3-group of halogenopropanes 1a and 1b (i.e. 'hydrolysis') was performed under atmospheric pressure in the presence of catalysts [20], and



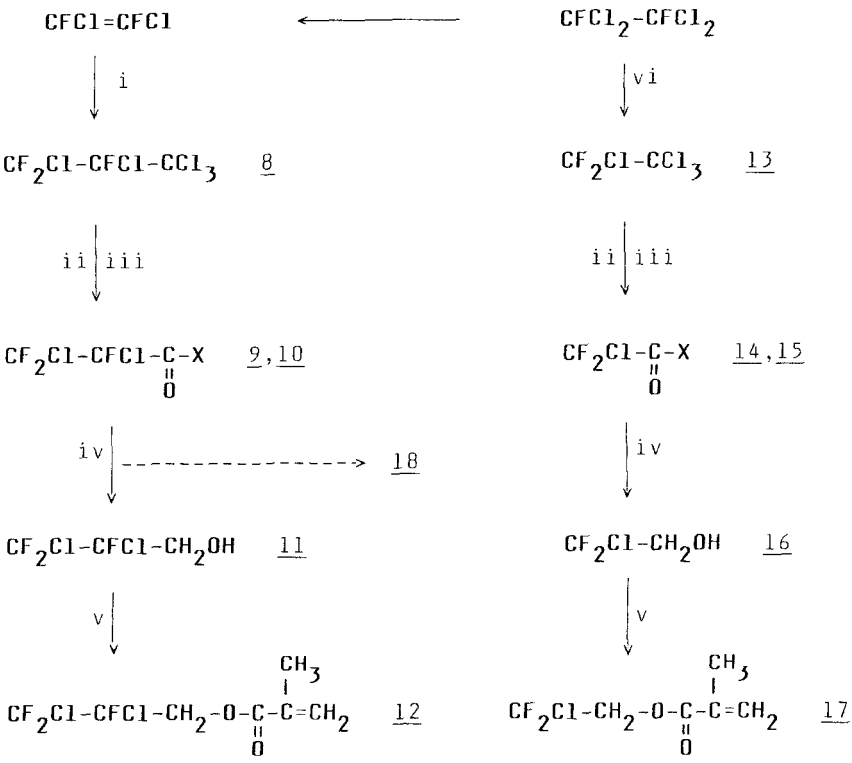
Scheme 1. Synthesis of fluoroalkanols based on chlorotrifluoroethylene.

stirring of the reaction mixture appeared to be an important reaction factor.

The reduction of halogenoesters 3a, 3b with sodium borohydride took place easily in refluxing diethyl ether [21] and no by-products, formed potentially by the reduction of the C-Cl bond, were identified even in the total conversion of the esters. Only at prolonged reaction time in the course of the reduction of ester 3a, 2,3,3,3-tetrafluoropropanol (7) began to appear in a small amount. Thus we concluded that compound 7 had been formed by a subsequent reduction reaction of fluoroalkanol 4a. Its identification was performed in the mixture with compound 4a by the NMR spectra. The mixture of chlorotetrafluoropropanols 4a and 4b was successfully separated by rectification. Acylation of the halogenopropanols with methacryloyl chloride took place readily in the presence of triethyl amine. Contrary to that, the acylation with acryloyl chloride afforded the corresponding acrylates 6a and 6b by refluxing the reactants in diethyl ether.

The synthesis of fluoroalkanols 11 and 16, starting from freon 112, and of their methacrylates 12 and 17, is depicted in Scheme 2. Halogenopropane 8, produced in a bench-plant process [11], contained *ca.* 35 % isomers, which were separated in a greater part in the following steps, *i.e.* oxygenative dechlorination in the CCl_3-group (acid chloride 9) and the preparation of methyl ester 10. The reduction of this ester with sodium borohydride took place almost chemo-specifically: before the complete conversion of the ester 10 in halogenopropanol 11 a small amount (2-5 %) of a by-product, probably 3-chloro-2,3,3-trifluoropropanol (18) (as deduced from ^{19}F NMR spectra of alkanol mixture), was detected by GLC in the reaction mixture. Acylation of halogenopropanol 11 with methacryloyl chloride was performed in the presence of triethyl amine.

The preparation of 1,1-difluorotetrachloroethane (13) as well as its oxygenative dechlorination to 2-chloro-2,2-difluoro-



9,14, X = Cl

10,15, X = OCH_3

$CF_2Cl-CHF-CH_2-OH$ 18

i $CFCl_3$, $AlCl_3$, 15-25 °C ; ii oleum 20 % , HgO ; iii MeOH ; iv $NaBH_4$, Et_2O ; v methacryloyl chloride , NEt_3 ; vi $AlCl_3$, 40-50 °C .

Scheme 2. Synthesis of fluoroalkanols based on 1,2-difluorotetrachloroethane.

acetyl chloride (14) and preparation of methyl ester 15 has been optimized formerly [12,20]. The former reduction of the ester 15 with sodium borohydride in methanol followed by subsequent extraction of the reaction mixture with chloroform [18] afforded relatively low yields of the halogenoethanol 16. More convenient appeared to be the reduction in a medium of diethyl ether [22], similarly as in the case of esters 3a, 3b and 10. Acylation of 2-chloro-2,2-difluoroethanol (16) was again performed in the presence of triethyl amine.

In the preparative reduction of esters 3a, 10 and 15 we observed a conspicuous difference in the rate of the reaction.

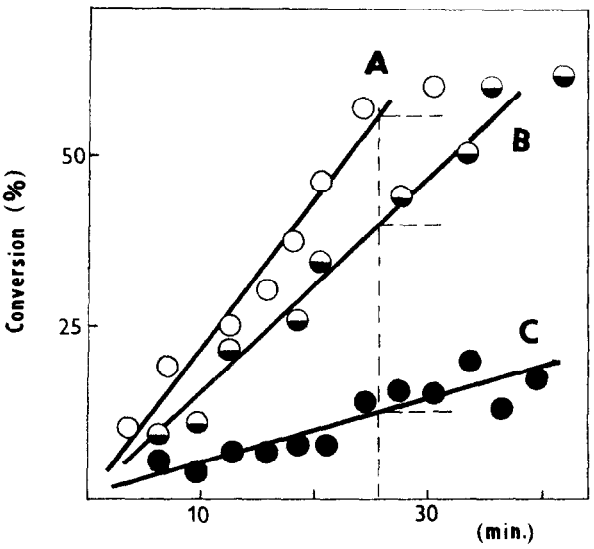


Fig. 1. Empirical kinetics of the sodium-borohydride reduction of esters 3a, 10 and 15.

A CF_2Cl-$COOCH_3$ (15) ⟶ 16

B CF_3-$CFCl$-$COOCH_3$ (3a) ⟶ 4a

C CF_2Cl-$CFCl$-$COOCH_3$ (10) ⟶ 11

We made an attempt to quantify the difference in the kinetics and to determine empirically the relative rates. The kinetic measurements were performed under the standardized conditions by the method of competitive reactions. Evaluations of product concentrations were performed chromatographically by means of calibration graphs. The results of measurements are shown in Fig. 1: at low conversion, the reductions approximately followed zero-order kinetics.

When considering the esters studied (3a, 10 and 15) as modifications of the model $X\text{-}CF_2\text{-}COOCH_3$, then the reactivity order will be the following:

X	Cl	CF_3	CF_2Cl
k_{rel}	4.5	3.5	1.0

The most probable factor affecting the reactivity of the esters in a complex-hydride reduction is the bulkiness of substituent X. In this respect the results show that the chlorine atom and the CF_3-group exhibit almost the same steric effect. On the other hand, the CF_2Cl-group containing a chlorine atom at the β-position with respect to the carbonyl group causes a four-fold decrease in the reaction rate in comparison with the former groups. We observed a similar steric effect in acid hydrolysis of methyl halogenopropanoates [23]. The presence of the group $X = CF_2Cl$ in model compounds 10, 19 and 20 analogously caused a three-fold decrease in the hydrolysis rate in

$X\text{-}CFCl\text{-}COOCH_3$ (10) $\quad$ $X\text{-}CHF\text{-}COOCH_3$ (19) $\quad$ $X\text{-}CCl_2\text{-}COOCH_3$ (20)

comparison with compounds containing the substituent $X = CF_3$. The complex-hydride reduction and, on the other hand, hydrolysis via an $A_{Ac}2$ mechanism of the halogenopropanoates, which we verified for this reaction [23], are evidently different reactions. From the point of view of a nucleophilic attack of the carbonyl-group carbon atom by a bulky agent, however, both the reactions are similar and apparently for that reason exhibit practically the same steric effect in the quantitative aspect.

EXPERIMENTAL

General comments and apparatus

All boiling points are uncorrected. The GLC techniques and apparatus used have been described before [13].

The new compounds 5a, 5b, 6a, 6b, 12 and 17 and a greater part of their synthetic precursors were characterized by elemental analyses and ^{1}H and ^{19}F NMR spectra (Tables 2 and 3). The NMR spectra were recorded in deuteriochloroform on a Varian XL-100/15 (CW, 100 and 94 MHz, respectively) and Tesla 567 (FT, 100 MHz) instruments (tetramethylsilane and $CFCl_3$ as internal standards, chemical shifts in ppm, coupling constants J in Hz).

Chemicals and compounds used

Sodium borohydride (Metallgesellschaft AG, Frankfurt). The solvents used were purified and dried by general methods. Halogenoalkanes 1, 1a, 1b, 8 and 13 were prepared according to the described procedures [10-13]. Halogenoalkanes 8 and 13 were converted to acid chlorides 9 and 14, respectively, after Refs. [11,20], which in turn gave the corresponding esters 10 and 15, respectively, by reaction with methanol. Methyl halogenopropanoate 10 for kinetic studies contained ca. 3 % of the isomeric methyl 2,2-dichloro- and 3,3-dichlorotrifluoropropanoate after rectification on a rotatory column (BR Glass Inc., Pasadena).

Oxygenative dechlorination (i.e. hydrolysis) of tetrachlorotetrafluoropropanes (1a, 1b)

General procedure

A mixture of halogenoalkane (0.5-0.6 mol), oleum (40-65 % of SO_3, 80-100 ml), mercuric oxide (1-2 g) and silver acetate (0.1-0.2 g) in a three-necked flask equipped with a gas-tight stirrer and a Vigreux column (80 cm) with a dephlegmator, was stirred and refluxed. Acid chlorides were collected in a temperature range of 50-61 ^{o}C. The distillate was then mixed with sulphuric acid (ca. 90 %, 10 ml) and after stirring 15 min. the acid-chloride layer was rectified on a packed column (ceramic saddles), b.p. 47-49.5 ^{o}C. The acid chlorides obtained were used for the preparation of esters 3 and 3a, respectively.

Table 2

NMR SPECTRA OF COMPOUNDS 3-7, 10-12 16 and 17

	Compound	Spectrum[a]	Character of signals[b]
3a	CF_3-CFCl-$COOCH_3$	B	d -80.3 (CF_3), $^3J_{FF}$ 7, q -132.8 (CFCl)
3b	CF_2Cl-CF_2-$COOCH_3$	B	t -70.8 (CF_2Cl), $^3J_{FF}$ 5, t -117.3 (CF_2)
4a	CF_3-CFCl-CH_2OH	A	d 4.11 (CH_2), $^3J_{HF}$ 16, s 3.45 (HO, 60 °C)
		B	d -80.5 (CF_3), tqa (dec. qa) -136.2 (CFCl), $^3J_{FF}$ 6
4b	CF_2Cl-CF_2-CH_2OH	A	t 4.08 (CH_2), $^3J_{HF}$ 14, s 3.45 (HO, 60 °C)
		B	m (dec. t) -70.8 (CF_2Cl), $^3J_{FF}$ 3, tt (dec. t) -122.3
5a	CF_3-CFCl-CH_2O-MA[c]	A	s 6.22 and s 5.69 (H_2C=C), d 4.70 (OCH_2), $^3J_{HF}$ 15, s 2.0 (CH_3)
		B	d -80.9 (CF_3), $^3J_{FF}$ 6, tqa (dec. qa) -134.4 (CFCl)
5b	CF_2Cl-CF_2-CH_2O-MA	A	s 6.22 and s 5.69 (H_2C=C), s 2.0 (CH_3), t 4.67 (OCH_2), $^3J_{HF}$ 13
		B	t -71.0 (CF_2Cl), $^3J_{FF}$ 4.5, tt (dec. t) -119.5 (CF_2)
6a	CF_3-CFCl-CH_2O-Acr[d]	A	d 6.42 (C=CH-), $^3J_{HH}$ 3, s 6.17 and 5.97 (CH_2=C), d 4.72 (OCH_2), $^3J_{HF}$ 16
		B	d -80.9 (CF_3), $^3J_{FF}$ 6, m -134.2 (CFCl)
6b	CF_2Cl-CF_2-CH_2O-Acr	A	d 6.58 (C=CH-), $^3J_{HH}$ 3, s 6.17 and d 5.99 (CH_2=C), t 4.65 (OCH_2),

			$^{3}J_{HF}$ 13
		B	s -71.1 (CF_2Cl), $^{3}J_{FF}$ ca. 2, t (dec. s) -119.6 (CF_2)
7	CF_3-CHF-CH_2OH	A	dm 4.75 (CHF), $^{2}J_{HF}$ 46, -CH_2- not identified (overlap with 4a)
		B	dd (dec. d) -78.1 (CF_3), $^{3}J_{FF}$ 12, $^{3}J_{HF}$ 12, m (dec. qa) -208.4 (CHF)
10	CF_2Cl-CFCl-$COOCH_3$	B	dd -63.5 and dd -68.3 (CF_2Cl), $^{2}J_{FF}$ 168, $^{3}J_{FF}$ 168, $^{3}J_{FF}$ 8 and 12, dd -126 (CFCl)
11	CF_2Cl-CFCl-CH_2OH	A	m 4.18 (CH_2), $^{3}J_{HF}$ 9, s 3.54 (HO 57 ^{o}C)
		B	d -65.7 (CF_2Cl), $^{3}J_{FF}$ 10, m (dec. t) -129.4 (CFCl)
12	CF_2Cl-CFCl-CH_2O-MA	A	s 6.27 and qt 5.7 (CH_2=C), d 4.8 (OCH_2), $^{3}J_{HF}$ 14, t 2.0 (CH_3)
		B	d -65.9 (CF_2Cl), $^{3}J_{FF}$ 10, m (dec. t) -127.5 (CFCl)
16	CF_2Cl-CH_2OH	A	s 4.6 (HO), t 4.0 (CH_2), $^{3}J_{HF}$ 11
		B	t -65.1 (CF_2Cl)
17	CF_2Cl-CH_2O-MA	A	s 6.17 and s 5.6 (CH_2=C), t 4.5 (CH_2), $^{3}J_{HF}$ 10, s 1.95 (CH_3)
		B	t -61.9 (CF_2Cl)

[a] A - ^{1}H NMR spectrum, B - ^{19}F NMR spectrum;
[b] signals: s singlet, d doublet, t triplet , qa quadruplet, q quasi, dec. ^{1}H decoupling;
[c] MA - methacryloyl; d Acr - acryloyl .

Table 3

ELEMENTAL ANALYSES OF SOME COMPOUNDS

Compound			Calculated/Found			
No.	Formula	Mol.wt.	% C	% H	% Cl	% F
3	$C_4H_3ClF_4O_2$	194.5	24.7/24.8	1.54/1.52	18.3/18.2	39.1/39.2
3a	$C_4H_3ClF_4O_2$	194.5	24.7/24.6	1.54/1.53	18.3/18.5	39.1/38.9
4	$C_3H_3ClF_4O$	166.5	21.6/21.8	1.80/2.01	21.3/20.9	45.7/45.9
4a	$C_3H_3ClF_4O$	166.5	21.6/21.8	1.80/1.92	21.3/21.0	45.7/45.4
4b	$C_3H_3ClF_4O$	166.5	21.6/21.6	1.80/1.70	21.3/21.1	45.7/45.5
5	$C_7H_7ClF_4O_2$	234.6	35.8/36.1	2.99/3.27	15.1/14.8	32.4/32.1
5a	$C_7H_7ClF_4O_2$	234.6	35.8/36.0	2.99/3.21	15.1/14.9	32.4/32.0
5b	$C_7H_7ClF_4O_2$	234.6	35.8/36.1	2.99/3.14	15.1/14.8	32.4/32.2
6	$C_6H_5ClF_4O_2$	220.5	32.6/32.3	2.28/2.32	16.1/16.2	34.5/34.1
6a	$C_6H_5ClF_4O_2$	220.5	32.6/32.8	2.28/2.37	16.1/15.9	34.5/34.2
6b	$C_6H_5ClF_4O_2$	220.5	32.6/32.9	2.28/2.44	16.1/15.8	34.5/33.9
11	$C_3H_3Cl_2F_3O$	183.0	19.7/20.0	1.64/1.67	38.8/38.3	31.2/30.9
12	$C_7H_7Cl_2F_3O_2$	250.9	33.5/33.6	2.79/2.92	28.3/27.9	22.7/22.7
16	$C_2H_3ClF_2O$	116.7	20.6/20.3	2.57/2.80	30.4/30.0	32.6/32.9
17	$C_6H_7ClF_2O_2$	184.6	39.0/38.9	3.93/4.11	19.2/19.0	21.0/21.0

Chlorotetrafluoropropanoyl chloride (2)

The starting tetrachlorotetrafluoropropane 1 (152.5 g, 0.6 mol) contained 48 and 36 % of the isomers 1a and 1b (1,1,1,3-tetrachlorotetrafluoropropane), respectively, and 16 % of other 3 isomers not possessing a CCl_3-group [10]. The yield of the product 2 was 90.7 g (76 %), b.p. 47-49.5 °C.

2-Chlorotetrafluoropropanoyl chloride (2a)

The starting 1,1,1,2-tetrachlorotetrafluoropropane (1a, 127 g, 0.5 mol) contained an admixture of two isomers (ca. 12 %) not possessing a CCl_3-group, which were unreactive under the hydrolysis conditions. The yield of acid chloride 2a was 80.1 g (80.5 %), b.p. 47-48.5 °C (Ref. [10] 48-50 °C).

Methyl chlorotetrafluoropropanoates 3, 3a

Acid chloride (2 or 2a, 0.3-0.4 mol) was added with stirring and outside-cooling with ice to methanol (1-1.5 mol) in a flask fitted with a reflux condenser. After refluxing for 3 h the mixture was washed with ice-water, dried over anhydrous magnesium sulphate and rectified on a packed column (wire spirals); GLC: poly(1,3-propanediol sebacate), 80 °C, 360 cm.

Methyl chlorotetrafluoropropanoate (3)

Mixed acid chloride 2 (79.6 g, 0.4 mol) yielded the product 3, yield 68.1 g (87.5 %), composition 74 % 3a, 26 % 3b, as a series of fractions in a b.p. range 91-94 °C with a changing content of isomeric esters 3a and 3b: e.g., the fraction of b.p. 91-91.3 °C contained 88 % 3a, and the fraction of b.p. 93.5-94 °C contained 66 % 3a (GLC, ^{19}F NMR).

Methyl 2-chlorotetrafluoropropanoate (3a)

Acid chloride 2a (59.7 g, 0.3 mol) yielded ester 3a, b.p. 91-92.5 °C (Ref.[10] 84.5-85 °C), yield 48.7 g (83.5 %), fraction purity 99.5 %, isomer 3a purity 99 %.

Sodium-borohydride reduction of esters. Chlorofluoroalkanols 4a, 4b, 11 and 16

Chlorotetrafluoropropanol (4)

A solution of the isomeric esters mixture 3 (70 g, 0.351 mol; 74 % 3a and 26 % 3b) in diethyl ether (80 ml) was added dropwise to a refluxed and

stirred mixture of sodium borohydride (11.8 g, 0.31 mol), diethyl ether (160 ml) and methanol (1 ml). After stirring and refluxing for 3 h the reaction mixture was cooled, decomposed with hydrochloric acid (50 ml, 1:1) and the water layer was twice extracted with diethyl ether (100 ml). Combined solutions were dried over anhydrous magnesium sulphate. Rectification on a packed column (ceramic saddles) yielded halogenopropanol 4, b.p. 93-102 ^{o}C (Ref. [9] b.p. 39-43/66 (^{o}C/kPa)), yield 41.6 g (71.2 %), purity 99 % (GLC: poly(1,3-propanediol sebacate), 250 cm, 90 ^{o}C); composition (by GLC): 71 % 4a, 29 % 4b.

2-Chloro-2,3,3,3-tetrafluoropropanol (4a)

Compound 4a was prepared by the above described procedure. Diethyl ether was removed by pre-rectification (b.p. of the distillate up to 50 ^{o}C) and the residual raw product was distilled under the reduced pressure (ca. 8 kPa). Rectification of the distillate under the nitrogen atmosphere afforded product 4a, b.p. 91-96 ^{o}C, yield 44.3 g (64.2 %), purity 99 %, isomer content: 5 % 4b . During prolonged reaction time (15 h and longer), a by-product was detected in the reaction mixture which was identified (^{1}H and ^{19}F NMR) as 2,3,3,3-tetrafluoropropanol (7).

3-Chloro-2,2,3,3-tetrafluoropropanol (4b)

Rectification of chlorotetrafluoropropanol 4 (70 % 4a, 30 % 4b) on a packed column (wire spirals) afforded a fraction of b.p. 107-108 ^{o}C (9.3 g), which contained 97 % of product 4b .

2,3-Dichloro-2,3,3-trifluoropropanol (11)

The reduction of ester 10 (40 g; 0.19 mol) with sodium borohydride (7.5 g, 0.197 mol) was performed as above (4a); the conversion of the starting ester 10 was monitored by GLC. Rectification on a packed column (wire spirals) under the reduced pressure afforded the product 11, b.p. 67-69/2 (^{o}C/kPa) (Ref. [9] b.p. 55-57/44 (^{o}C/kPa)), 24.7 g (71 %), purity 99 %, isomer composition: 96 % 11, 4 % 2 minority isomers; GLC: Carbowax 6000, 360 cm, 180 ^{o}C.

2-Chloro-2,2-difluoroethanol (16)

Methyl 2-chloro-2,2-difluoroacetate (15, 30 g, 0.208 mol) was reduced with sodium borohydride as above (11). Rectification on a packed column (wire spirals) afforded product 16, b.p. 95-96 ^{o}C (Ref. [16] b.p.

95-96 ^{O}C), yield 18.9 g (78.2 %), purity 99 %, GLC: poly(1,4-butanediol succinate), 360 cm, 130 ^{O}C.

Methacrylates of fluoroalkanols 4a, 4b, 11 and 16

General procedure

A solution of triethyl amine and methacryloyl chloride (1.05 chemical equivalent) in diethyl ether was added dropwise to a stirred mixture of halogenoalkanol (1 equiv.) and diethyl ether, the reaction temperature being kept at 10-20 °C. The mixture was then stirred for 2 h at room temperature, and after that an equal volume of water dissolving the precipitate was added. The organic layer was washed with water and, when necessary, with a water solution of sodium hydrogen carbonate to a neutral reaction, then dried over anhydrous magnesium sulphate. Ether was distilled off from a water bath and the residual raw product was rectified on a packed columns (ceramic saddles, wire spirals, respectively). All operations were performed in the presence of a polymerisation inhibitor (octyl pyrocatechol, 1,1-diphenyl-2-picryl hydrazyl).

Chlorotetrafluoropropyl methacrylate (5a, 5b)

Reaction of chlorotetrafluoropropanol 4 (23 g, 0.138 mol; isomer 4a 64 %, 4b 36 %) yielded product 5 as a mixture of isomers 5a and 5b (62 and 38 %, respectively, by NMR); the main fraction b.p. 51-54/2.1 (^{O}C/kPa), yield 21.1 g (65.2 %), purity 99 % (GLC: Carbowax 6000, 250 cm, 130 ^{O}C).

2-Chloro-2,3,3,3-tetrafluoropropyl methacrylate (5a)

Halogenoalkanol 4a (24.1 g, 0.146 mol) afforded product 5a; the main fraction b.p. 51-53/2.1 (^{O}C/kPa), yield 21 g (61.4 %), purity 99 % (GLC).

3-Chloro-2,2,3,3-tetrafluoropropyl methacrylate (5b)

Halogenoalkanol 4b (6.2 g, 37.2 mmol) afforded methacrylate 5b, which was isolated by distillation. The main fraction b.p. 52-54/2.1 (^{O}C/kPa), yield 5.08 g (58.2 %), purity 97 %.

2,3-Dichloro-2,3,3-trifluoropropyl methacrylate (12)

Halogenopropanol 11 (30 g, 0.164 mol) afforded methacrylate 12, the main fraction b.p. 25-27/0.013 (^{O}C/kPa), yield 31.2 g (75.8 %), purity 98.5 % (GLC: poly(1 4-butanediol succinate), 360 cm, 158 ^{O}C).

2-Chloro-2,2-difluoroethyl methacrylate (17)

Halogenoethanol 16 (21.6 g, 0.185 mol) afforded the corresponding methacrylate 17, the main fraction b.p. 46-48/2.4 (^{O}C/kPa), yield 26.7 g (78.8 %), purity 97.5 % (GLC: see compound 12, 138 ^{O}C).

Chlorotetrafluoropropyl acrylate (6a, 6b)

A mixture of halogenopropanol 4 (10 g, 60.1 mmol); isomers 4a 64 %, 4b 36 %) and acryloyl chloride (7.1 g, 78.5 mmol) and diethyl ether (15 ml) was refluxed for 2 h in a nitrogen atmosphere. After cooling to r.t. diethyl ether (10 ml) was added and the solution was 3 times washed with water (10 ml). The organic layer was dried over anhydrous magnesium sulphate, taken down, and the filtrate was rectified on a packed column (wire spirals). Product 6 was taken in a temperature range of 53-56/2.66 (^{O}C/kPa), yield 10.2 g (74.9 %), purity 96 %, isomer content: 2-chloro-2,3,3,3-tetrafluoropropyl acrylate (6a) 66 %, 3-chloro-2,2,3,3-tetrafluoropropyl acrylate (6b) 34 % (GLC: Carbowax 6000, 240 cm, 110 ^{O}C).

Kinetics of the borohydride reduction of esters 3a, 10 and 15

A mixture of two esters was added to the boiling and stirred mixture of diethyl ether (25 ml), methanol (0.5 ml), sodium borohydride (0.6 g, 15.9 mmol) and diglyme (1.5 g, 11.2 mmol, internal standard). Samples of the reaction mixture were withdrawn through a septum, immediately decomposed with a small amount of hydrochloric acid (1:1) and subsequently analysed by GLC (see compound 11). Increase in halogenoalkanol concentrations in the

Mixture of esters	Ester (g/mmol)		
	3a	10	15
1	0.92/4.73	1.0/4.74	-
2	0.92/4.73	-	0.68/4.71
3	-	1.0/4.74	0.68/4.71

reaction mixture was calculated relatively to the diglyme concentration by means of calibration graphs. Each competitive reaction (see the Table) was performed in two runs. The points in Fig. 1 thus represent a mean of four experimental values.

ACKNOWLEDGEMENTS

The spectral measurements were carried out in the Laboratory of NMR spectroscopy (Dr. P. Trška, Head); the elemental analyses were performed in the Laboratory of organic analysis (Dr. L. Helešic, Head), both of the Prague Institute of Chemical Technology, Prague. The authors gratefully acknowledge their co-operation.

REFERENCES

1 M.J. Bowden, Materials for Microlithography, ACS Symposium Series 266, Amer. Chem. Society, Washington, 1984, p. 10.
2 B. Bednář, A.V. Jelcov, J. Zachoval, J. Králíček and T.A. Jurje, Světočuvstvitělnyje poliměrnyje matěrialy (Light-Sensitive Polymer Materials), Chimija, Leningrad, 1985.
3 O. Paleta and V. Dědek, Sborník Vys. Školy Chem.-Technol. v Praze, S 15 (1986) 69.
4 B. Bednář, J. Devátý, J. Králíček and J. Zachoval, Org. Coat., Appl. Polym. Sci. Proc., 48 (1983) 711.
5 B. Bednář, V. Maroušek, J. Zachoval and O. Paleta, Czech. Pat. Appl., PV 8243-88.
6 G.N. Taylor, Solid State Technol., (1984), 124.
7 B. Boutevin, G. Rigal, A. Rousseau and D. Bosc, J. Fluorine Chem., 38 (1988) 47.
8 L.S. German and I.L. Knunyants, Zh. Vses. Khim. O-va Im. D.I. Mendeleeva, 11 (1966) 354.
9 Imperial Chemical Industries, Ltd., Fr. Pat. 1 496 633 (1967); Chem. Abstr., 69 (1968) 51584.
10 O. Paleta, A. Pošta and K. Tesařík, Collect. Czech. Chem. Commun., 36 (1971) 2257.
11 O. Paleta, A. Pošta and F. Liška, Sborník Vys. Školy Chem.-Technol. v Praze, C 25 (1978) 105.
12 O. Paleta, F. Liška, A. Pošta and V. Dědek, Collect. Czech. Chem. Commun., 45 (1980) 104.
13 O. Paleta, J. Kvíčala, J. Günter and V. Dědek, Bull. Soc. Chim. Fr. (1986) 920.

14 D. Osteroth, 'Chemie und Technologie aliphatischer fluororganischer Verbindungen', F. Enke, Stuttgart, 1964, p.55.
15 M. Hudlický, 'Chemistry of Organic Fluorine Compounds', J. Wiley, New York, 1976, p. 180.
16 R.M. Murrel and R.O. Pierce, Ind. Eng. Chem., 49 (1957) 1241.
17 B. Boutevin and Y. Pietrasanta, Europ. Polym. J., 12 (1975) 231.
18 K. Klouda, Diploma Dissertation, Prague Institute of Chemical Technology, Prague, 1976.
19 J. Kvíčala, O. Paleta and V. Dědek, J. Fluorine Chem., 43 (1989) 155.
20 O. Paleta, A. Pošta and I. Hemer, Czech. Pat. 118 604 (1964).
21 O. Paleta, L. Štěpán, J. Svoboda and V. Dědek, Czech. Pat. 204 892 (1980).
22 O. Paleta, A. Danda and V. Dědek, Czech. Pat. 246 495 (1986).
23 O. Paleta, J. Kvíčala and V. Dědek, Collect. Czech. Chem. Commun., 48 (1983) 2805.