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PHOTOCHEMICAL REDUCTION OF CARBON-HALOGEN BONDS. 3*. REGIOSELECTIVITY OF THE REACTION IN FLUORINATED HALOGENOPROPANOATES

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SUMMARY

The ester group exhibits a strong directive effect in the photochemical reduction of a carbon-halogen bond and directs the reduction in perhalogenated chlorofluoropropanoates of the type CFXY-CClZ-COOR (X,Y,Z = Cl,F) to the α-position in the acyl part of an ester. The reduction takes place with the same regioselectivity even in esters $CFCl_2$-CHCl-COOR (10). In esters containing an α -CCl_2- group the reductions to the first and the second stages can be separated and the individual reduction products can be obtained preparatively. The α C-F bond is more difficult to reduce and therefore in the ester $CFCl_2$-CHF-COOR (11) the β C-Cl bond was reduced specifically and in the ester CF_2Cl-CHF-COOR (12) both the α C-F bond and the β C-Cl bond were reduced parallely. The relative reactivity of fluorinated halogenopropanoates with an α C-Cl bond showed only small differences in the reduction with 2-propanol in the presence of acetone as a sensitiser; the quantum yield Φ reached values of about 28-35 under kinetic measurements and thus proved the existence of a chain radical mechanism.

*For Part 1 see Ref. [1], for Part 2 see Eef. [2].

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INTRODUCTION

The reduction of a carbon-halogen bond initiated by UV radiation has been recorded for different structural types. The substitution of a halogen atom by hydrogen in this way can be performed in saturated aliphatic structures [1-3], in alicyclic structures [4,5], on multiple bonds [4,5], on an aromatic ring [5-7], in aryl-aliphatic structures [8], and on a heterocyclic ring [9]. In the first row aliphatic alcohols [1-5,7-9] and hydrocarbons [6] sometimes served as hydrogen donors. The introduction of the hydrogen atom into a molecule of a highly halogenated compound is of synthetic [1-4,7] as well as ecological [5,8] importance, because photochemical dehalogenation could become one of the degradation processes of otherwise stable chlorinated compounds.

The photochemically - initiated reduction is an advantageous synthetic method, especially in the case of polyhalogenated aliphatic compounds [1,3] offering the possibility of syntheses of compounds obtainable otherwise by more difficult synthetic routes (see publications in Ref. [1]). Aliphatic alcohols are used with advantage as hydrogen donors. In the photo-reduction, the specific reactivity of different halogen substituents or the highly selective reactivity of the same carbon-halogen bonds at different places in a molecule, which can be quite specific, is exploited.

In our previous publication [1] we showed that under preparative conditions the photochemically initiated reduction of the C-Cl bond in the grouping -CFCl- takes place specifically at the α-position to an ester group. The maximum quantum yields in the case of three esters exceeded the value of 200. A strong directive effect of an ester group in the reduction was observed [10-12], too, in fluorinated esters containing groupings $-CF_2-$ or -CHF- at α-positions:

$$R\text{-}CF_2\text{-}\underset{\downarrow}{C}X\text{-}COOR \qquad \begin{matrix} X = H, F \\ R = F, \text{perfluoroalkyl} \end{matrix}$$
$$\qquad\quad F$$

The photo-reduction of halogenoesters with perfluorinated

acyl moieties proceeds stepwise, and in the case of trifluoroacetates all three α C-F bonds can be reduced [12] in this way. However, quantum yields of the reduction of such esters in hexamethylphosphortriamide were rather low and reached values of the order of 10^{-2}.

SELECTIVITY OF THE REDUCTION IN FLUORINATED HALOGENOPROPANOATES

According to the previous publications [1,10,12] it can be concluded that the carboxylic or ester groups exhibit a strong directive effect, by which a high selectivity of the photochemical reduction of the carbon-halogen bonds in fluorinated esters is guaranteed. In this connection we were interested to find out how strongly the selectivity of the α-position-reduction is influenced by the composition of the β-trihalogenomethyl group in situations when different numbers of fluorine atoms were involved. We used 2-propanol as a suitable source of hydrogen, and this reducing agent was oxidised to acetone stoichiometrically during the reaction:

$$\mathrm{CFXY\text{-}\underset{Cl}{\underset{|}{C}}Z\text{-}COOR} + (CH_3)_2CH\text{-}OH \xrightarrow{h\nu} \mathrm{CFXY\text{-}\underset{H}{\underset{|}{C}}Z\text{-}COOR} + HCl + (CH_3)_2C{=}O$$

X,Y,Z = Cl,F

The directive effect of the ester groups versus the reactivity of the β-trihalogenomethyl group under comparable conditions, when acetone was not added into the reaction mixture initially, is shown in Scheme 1. In all starting compounds 1-5 of the reactions /1/-/5/ the reduction takes place at the α-position related to the ester group. If in a starting ester two α C-Cl bonds are present, then the second α C-Cl bond is reduced specifically without regard to the composition of the β-trihalogenomethyl group, i.e. no competitive reaction with β C-Cl bonds was observed. On the contrary, the reduction of an α C-F bond is more difficult in comparison with the C-Cl one. This probably is the reason why the

Regioselectivity of the reduction of some chlorofluoropropanoates in 2-propanol

Reaction No.	Starting compound[a]	hν, 2-PrOH →	Reduction to the first stage	hν, 2-PrOH →	Reduction to the second stage	Figure No.
/1/	$CF_3-CCl(Cl)-COOR$ **1**		$CF_3-CH(Cl)-COOR$ **8**		CF_3-CH_2-COOR **15**	-
/2/	$CF_2Cl-CCl(Cl)-COOR$ **2**		$CF_2Cl-CH(Cl)-COOR$ **9**		CF_2Cl-CH_2-COOR **16**	1
/3/	$CFCl_2-CCl(Cl)-COOR$ **3**		$CFCl_2-CH(Cl)-COOR$ **10**		$CFCl_2-CH_2-COOR$ **17**	2
/4/	$CFCl_2-CF(Cl)-COOMe$ **4**		$CFCl(Cl)-CHF-COOMe$ **11**		$CHFCl-CHF-COOMe$ **18**	3
/5/	$CF_2Cl-CF(Cl)-COOBu$ **5**		$CF_2Cl-CHF-COOBu$ **12**		no reaction	-

[a] R - $CH(CH_3)_2$, Me - CH_3 , Bu - $CH_2(CH_2)_2CH_3$

Scheme 1.

reduction did not take place in ester 12 (reaction /5/) under similar conditions as in reactions /1/-/4/. On the other hand, however, with the grouping of halogen bonds in $CFCl_2$-CHF-COOR (11,13) the reduction takes place in the β-position (reaction /4/) and the directive effect of the ester group is no longer operative.

Kinetic curves of some reduction reactions of substrates containing at least three C-Cl bonds in the acyl part are shown in Figs. 1-3. Fig. 1 shows not only the selective course of the reduction to the first and the second stages (reaction /2/) at the α-position but also a great difference in the rate of the reduction to the second stage. Thus it is possible to reach a separate reduction of substrate to the individual reduction products 9 or 16 under preparative conditions with almost a 100 % conversion to either of them. As seen also from Fig. 2 in the case of reaction /3/ the reduction to the second stage (product 17) follows after an almost complete conversion of substrate 3 to product 10; there is only a slight overlap of the kinetic curves. Therefore it is necessary under the preparative conditions to follow the course of the reduction analytically (e.g. by GLC) to obtain relatively pure products 10 or 17. In contrast to this case, the kinetics of reaction /4/ in Fig. 3 shows that the concentration curves of reduction products 11 and 18 and of substrate 4 overlap one another. At the maximum concentration of the first reduction product 11 substrate 4 is still present in the reaction mixture and some small amount of the subsequent reduction product 18 is present too; evidently, the reduction of ester 4 is not limited to consecutive reduction stages, and product 11 can be obtained only in a mixture with compound 4 or 18, or with both.

NON-SPECIFIC REDUCTION

In connection with reaction /5/ (Scheme 1) we tested the strength of the directive effect of the ester group in the reduction of the α C-F bond in competition with the β C-Cl bond in the CF_2Cl- group. As a model compound we used ester

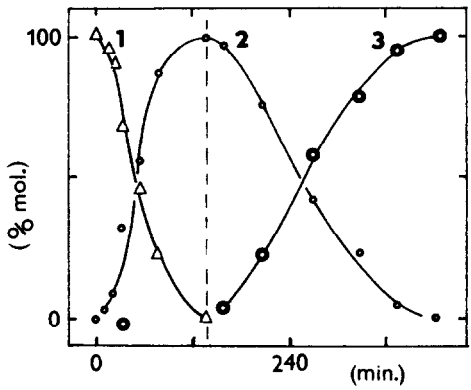


Fig. 1.

Time dependence of the reduction of ester 2 (reaction conditions see Experimental):

1: $CF_2Cl-CCl_2-COOR$ (2)
2: $CF_2Cl-CHCl-COOR$ (9)
3: CF_2Cl-CH_2-COOR (16)

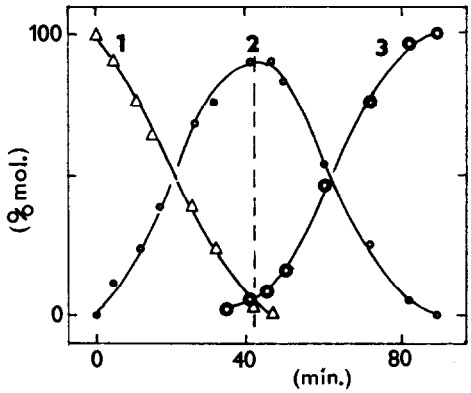


Fig. 2.

Time dependence of the reduction of ester 3 (reaction conditions see Experimental):

1: $CFCl_2-CCl_2-COOR$ (3)
2: $CFCl_2-CHCl-COOR$ (10)
3: $CFCl_2-CH_2-COOR$ (17)

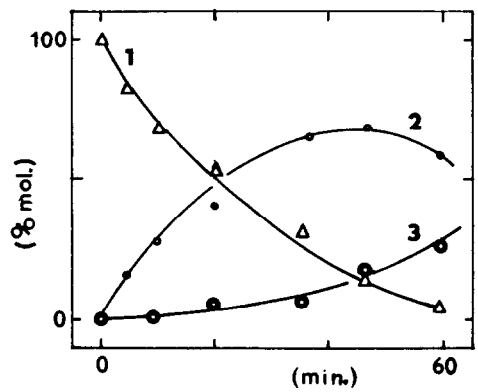


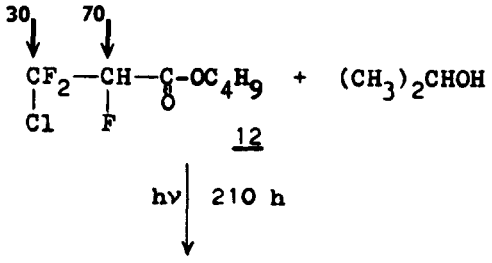
Fig. 3.

Time dependence of the reduction of ester 4 (reaction conditions see Experimental):

1: $CFCl_2-CFCl-COOMe$ (4)
2: $CFCl_2-CHF-COOMe$ (11)
3: $CHFCl-CHF-COOMe$ (18)

R = $CH(CH_3)_2$

12. The difficulty of this reduction (Scheme 2) is documented by an extraordinary long reaction time and low quantum yields that are more than four orders of magnitude than our former ones [1] under similar conditions. The structures of the products 14,16,19,20 show at the same time that in acidic media the re-esterification of the original butyl ester took place, contrary to the former [1] fast preparative reductions where no re-esterification was observed.



		Preparative yield (%)	Approximate quantum yield (Φ)
14	CF_2Cl-CHF-$COOCH(CH_3)_2$	23	0.02
16	CF_2Cl-CH_2-$COOCH(CH_3)_2$	14	0.01
19	CHF_2-CH_2-$COOCH(CH_3)_2$	11	0.01
20	CHF_2-CHF-$COOCH(CH_3)_2$	3	0.003

Scheme 2

The products 16 and 20 were formed as a mixture by a non--regiospecific reduction of halogen bonds in the starting ester 12. Compound 19 can be formed by a subsequent reduction reaction of products 16 and 20. With the presumption of an approximately equal reactivity of these products in the subsequent reduction, an approximate 70:30 reactivity ratio of the α C-F bond and the β C-Cl bond in compound 12 is obtained, i.e. α C-F bond reactivity was predominant. The structures of the products 19 and 20 were checked by mass spectra only, because these reaction mixture components were not separated successfully by GLC.

SENSITISATION OF THE REDUCTION WITH ACETONE

As has been mentioned, acetone is a stoichiometric product of the reduction in 2-propanol and its concentration

is increased with the increasing amount of the products. We observed formerly [1] that the addition of acetone in a greater amount to the reaction mixture lowers the rate of a preparative reaction. Contrary to this fact, the presence of acetone in the reaction mixture under kinetic conditions and in a relatively low concentration causes acceleration of the reduction, i.e. acetone acts as a sensitiser. The situation is shown in Fig. 4: the reaction rate, as represented by the slope of the linear part of the time dependence is increased gradually with the increasing initial concentration of acetone (and at constant starting concentration of the substrate 7). However, the rate of the reduction reaches a limit value at a certain concentration of acetone, and a greater amount of acetone in the solution no longer has an accelerating effect on the reaction. It follows that under such conditions the radiation is absorbed totally by acetone acting as a sensitiser. Fig. 5 shows the connection between the limiting rate, or quantum yield Φ of the reduction, and the concentration of acetone.

The relative reactivity of the individual esters 1,2,3,7 and 21 all containing α C-Cl bonds, was tested under such an initial concentration of acetone that a total absorption of monochromatic light of 254 nm with this sensitiser was guaranteed. From the linear kinetic dependences of the pseudo-zero

TABLE 1

Relative reactivity of some pentahalogenated esters in the reduction reaction (slopes of the zero-order kinetic lines (Fig. 6) are given in quantum yields Φ)

	Ester	Φ
7	$CF_2Cl-CFCl-COOCH(CH_3)_2$	35
21	$CF_3-CFCl-COOCH(CH_3)_2$	33
1	$CF_3-CCl_2-COOCH(CH_3)_2$	32
3	$CFCl_2-CCl_2-COOCH(CH_3)_2$	30
2	$CF_2Cl-CCl_2-COOCH(CH_3)_2$	28

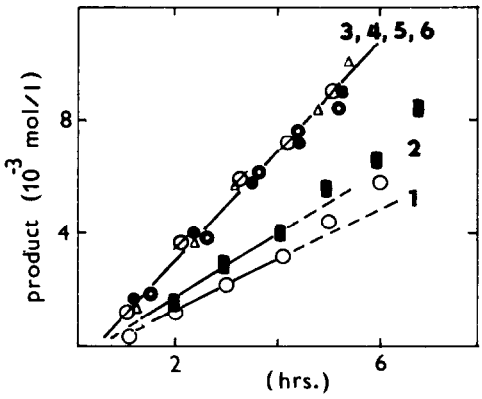


Fig. 4.

Rate dependence of the photoreduction of ester CF_2Cl-$CFCl$-COOR (7, 0.04 mol/l) on acetone concentration (mol/l, conditions see Fig. 1):

1 - ○ : 0.008
2 - ▮ : 0.011
3 - ● : 0.018
4 - △ : 0.024
5 - ◘ : 0.034
6 - ⌀ : 0.043

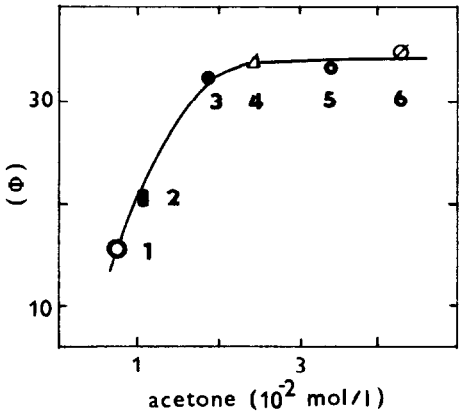


Fig. 5.

Dependence of quantum yield Φ of the reaction in Fig. 4 on acetone concentration (point marking see Fig. 4)

R - $CH(CH_3)_2$

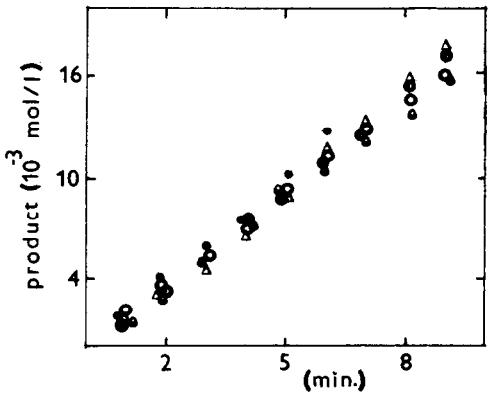


Fig. 6.

Rates of the sensitised photoreduction of esters 1, 2, 3, 7 and 22 (0.05 mol/l, acetone 0.03 mol/l; conditions see Fig. 4):

◐ CF_3CCl_2-COOR (1)
• CF_2Cl-CCl_2-COOR (2)
◎ $CFCl_2$-CCl_2-COOR (3)
• CF_2Cl-$CFCl$-COOR (7)
▲ CF_3-$CFCl$-COOR (21)

order (Fig. 6) the quantum yields of the reduction to the first stage were calculated (Table 1). The values show that the differences in reactivity as characterised by quantity Φ are relatively low, the extent of values Φ being about 20 % the maximum value and approaching and experimental error (ca. 10 %). Thus it can be concluded that the esters tested react approximately at the same rate under sensitisation with acetone, and the high quantum yields (Φ = 28-35) again verify a chain mechanism.

EXPERIMENTAL

General comments and apparatus

All boiling points are uncorrected. Gas chromatography was performed on a Chrom 41 (Laboratorní přístroje, Praha) analytical instrument (FID, stainless steel columns 0.3 x 240 and 0.3 x 380 cm, nitrogen, support Chromaton N-AW-DMCS (Lachema, Brno) packed with silicone elastomer E 301 and poly-(1,4-butanediol succinate).

The new compounds 8-20 were characterised by NMR spectra (^{1}H and ^{19}F), elemental analyses and some of them (Table 4) by mass spectroscopy. The elemental analyses and NMR measurements are summarised in Tables 2 and 3. The NMR spectra were recorded in deuteriochloroform on Varian XL-100/15 (100 MHz, CW) and Bruker AM-400 instruments (400 MHz, FT; tetramethylsilane and $CFCl_3$ as internal standards, chemical shifts in ppm, coupling constants J in Hz). The mass spectra were scanned on a Gas--Chromatograph - Mass Spectrometer tandem LKB 9000 (single focus, 70 eV, helium; GLC inlet via glass column 0.23 x 250 cm packed with Carbowax 20 M on Chromaton N-AW) and JEOL DX 303/DA 500 (single focus, 70 eV) apparatus.

Chemicals used

2-Propanol was dried and purified as previously [1]. Butyl- and (2-propyl)-2,3-dichloro-2,3,3-trifluoropropanoate (5,7) were prepared according to the described procedures [15, 16]; both esters 5 and 7 contained about 5 % of two other

TABLE 2

Elemental analyses of some compounds (for analyses of compounds 4,5 and 7 see Ref. [15])

Compound			Calculated/Found			
No.	Formula	Mol.wt.	% C	% H	% Cl	% F
1	$C_6H_7Cl_2F_3O_2$	239.0	30.1/30.0	2.95/2.91	29.7/29.8	23.8/23.5
2	$C_6H_7Cl_3F_2O_2$	255.5	28.2/28.4	2.76/2.96	41.6/41.3	14.9/15.1
3	$C_6H_7Cl_4FO_2$	271.9	26.5/26.2	2.60/2.64	52.2/52.7	6.99/6.67
6	$C_6H_7Cl_3F_2O_2$	255.5	28.2/28.6	2.76/2.98	41.6/41.7	14.9/14.3
8	$C_6H_8ClF_3O_2$	204.6	35.2/35.2	3.94/3.95	17.3/17.6	27.9/27.4
9	$C_6H_8Cl_2F_2O_2$	221.0	32.6/32.2	3.65/3.69	32.1/32.1	17.2/17.3
10	$C_6H_8Cl_3FO_2$	237.5	30.3/30.6	3.40/3.63	44.8/45.1	8.00/8.06
11	$C_4H_4Cl_2F_2O_2$	133.0	24.9/25.1	2.09/2.31	36.7/35.9	19.7/20.3
12	$C_7H_{10}ClF_3O_2$	218.6	38.5/38.7	4.62/4.81	16.2/16.4	26.1/26.3
13	$C_6H_8Cl_2F_2O_2$	221.0	32.6/32.4	3.65/3.84	32.1/31.8	17.2/17.8
14	$C_6H_8ClF_3O_2$	204.6	35.2/35.5	3.94/4.14	17.3/17.2	27.9/28.0
16	$C_6H_9ClF_2O_2$	184.6	39.0/39.7	3.82/4.29	19.2/18.7	20.6/21.2
17	$C_6H_9Cl_2FO_2$	203.0	35.5/35.8	4.74/4.36	34.9/34.8	9.36/10.0
21	$C_6H_7ClF_4O_2$	222.6	32.4/32.2	3.18/3.31	15.9/16.2	34.1/33.8
22	$C_6H_8F_4O_2$	183.7	38.3/38.3	4.29/4.28	-	40.4/40.2

TABLE 3

NMR spectra of compounds 1-3, 6-8, 10-12, 16 and 17 (^{1}H NMR signals of ester groups are not presented)

	Compound	Spectrum[a]	Character of signals[b,c]
1	CF_3-CCl_2-COOR	B	s -76
2	CF_2Cl-CCl_2-COOR	B	s -60.9
3	$CFCl_2$-CCl_2-COOR	B	s -59.1
6	$CFCl_2$-CFCl-COOR	B	d -65 (1), ^3J(F-F) 17.5, d -118.5 (1)
7	CF_2Cl-CFCl-COOR	B	dd -63.9 (1), dd -66.5 (1), ^2J(F-F) 170, ^3J(F-F) 11,5, t -125.5
8	CF_3-CHCl-COOR	A_1	q 5.68 (1), ^3J(H-F) 6.5
		B_1	d -72.1
10	$CFCl_2$-CHCl-COOR	A_1	d 4.83 (1), ^3J(H-F) 10.3
		B_1	d -61.1
11	$CFCl_2$-CHF-COOMe	A_1	dd 4.2 (1), ^2J(H-F) 45, ^3J(H-F) 8
		B_1	dd -66 (1), dd -183.8 (1), ^3J(F-F) 23
12	CF_2Cl-CHF-COOBu	A	dt 5.1 (1), ^2J(H-F) 46, ^3J(H-F) 7
		B	ddd -63.2 (1), ddd -64.2 (1), ^2J(F-F) 172, ^3J(F-F) 17; dt - 195.3
13	$CFCl_2$-CHF-COOR	see compd. 11	
14	CF_2Cl-CHF-COOR	A_1	dt 5.08 (1), ^2J(H-F) 47, ^3J(H-F) 6
		B_1	ddd -62.6 (1), ddd -64 (1), ^2J(F-F) 174, ^3J(F-F) 17; dt -194.85
16	CF_2Cl-CH_2-COOR	A_1	t 3.47 (2), ^3J(H-F) 12.3
		B_1	t -49.9
17	$CFCl_2$-CH_2-COOR	A_1	d 3.54 (2), ^3J(H-F) 14.1
		B_1	t -51
18	CHFCl-CHF-COOMe	A	s 3.9 (3); ddd 5.2 (1), ^2J(H-F) 45, ^3J(H-H) 8, ^3J(H-F) 16; ddd 6.5 (1), ^3J(H-H) 2, ^2J(H-F) 48, ^3J(H-F) 13
		B	ddd -146 (1), ^3J(F-F) 15; ddd -149 (1), ^3J(F-F) 20; ddd -202.4 (1), ^2J(H-F) 48, ^3J(H-F) 13, ^3J(F-F) 15;

(Continued)

TABLE 3 (cont.)

ddd -204.3 (1)

R - $CH(CH_3)_2$, Me - CH_3 , Bu - $CH_2CH_2CH_2CH_3$
A_1,B_1 - measured on Bruker spectrometer.
[a] A ^1H NMR spectrum, B ^{19}F NMR spectrum.
[b] Signals: s singlet, d doublet, t triplet, q quartet.
[c] For the NMR spectra of compounds 9, 13 and 22 see Ref. [1].

TABLE 4

Mass spectra of compounds (13, 19, 20, 22)
(mass/relative intensity, ionic species)

Compound formula (mol. wt)	Principal ionic species[a]
13 $C_6H_8Cl_2F_2O_2$ (220)	205/5 $(CFCl_2CHFCO_2C_2H_4)^+$, 179/3 $(CFCl{=}CHFCO)^+$, 133/2 $(CFCl_2CHF)^+$, 101/4 $(CFCl_2)^+$, 98/8 $(C_2HCl{-}F_2)^+$, 83/3 $(CHCl_2)^+$, 79/1 $(C_2HClF)^+$, 67/3 $(CHClF)^+$, 63/3 $(C_2HF_2)^+$, 60/2 $(CHFCO)^+$, 59/3 $(C_3H_7O)^+$, 43/100 $(C_3H_7)^+$
19 $C_6H_{10}F_2O_2$ (152)	137/5 $(CHF_2CH_2CO_2C_2H_4)^+$, 117/11 $(CHF{=}CHCO_2C_2H_4)^+$, 111/16 $(CHF_2CHFCO)^+$, 93/100 $(CHF_2CH_2CO)^+$, 73/18 $(CHF_2CH_2CO)^+$, 73/18, 65/17 $(CHF_2CH_2)^+$, 59/22 $(C_3H_7O)^+$, 45/18 $(C_2H_2F)^+$, 43/93 $(C_3H_7)^+$
20 $C_6H_9F_3O_2$ (170)	156/4 $(CHF_2CHFCO_2C_2H_4)^+$, 135/5, 129/4, 111/48 $(CHF_2CHFCO)^+$, 91/9 $(C_2H_2F_2CO)^+$, 83/9 $(CHF_2CHF)^+$ 77/9, 69/10, 59/8, 57/13 $(C\,H\,CO)^+$, 56/13, 45/52 $(C_2H_2F)^+$, 43/65 $(C_3H_7)^+$, 28/100 $(CO)^+$
22 $C_6H_8F_4O_2$ (188)	173/16 $(CF_3CHFCO_2C_2H_4)^+$, 129/36 $(CF_3CHFCO)^+$, 101/34 $(CF_3CHF)^+$, 82/7 $(C_2HF_3)^+$, 69/17 $(CF_3)^+$, 60/6 $(CHFCO)^+$, 59/5 $(C_3H_7O)^+$, 51 $(CHF_2)^+$, 45/22 43/100 (C_3H_7)

[a] Assumed structures.

isomers. Methyl- and (2-propyl)-2,3,3-trichloro-2,3-difluoropropanoate (4,6) were prepared after Ref. [15]: A higher boiling fraction of acid halides from acidic oxygenative dechlorination of trichloromethylpropanes [16] was rectified on a packed column and 2,3,3-trichloro-2,3-difluoropropanoyl chloride was collected, b.p. 126-127 °C, which was used for the preparation of the esters 4 and 6; both esters contained 3-6 % of the isomeric 2,2,3-trifluoro-3,3-difluoropropanoate. (2-Propyl)-2-chlorotetrafluoropropanoate (21) was prepared after Ref. [1].

Synthesis of (2-propyl)-2,2-dichlorotrihalogenopropanoates 1-3

The former synthesis [15] was modified in the following manner: 1,1,1,2,2,3,3-Heptachloropropane was obtained in yields 72-76 %. Its dehydrochlorination to hexachloropropene was performed with potassium hydroxide in methanol at 14-18 °C. The conversion was followed by GLC.

(a) 1,1,2-Trichloro-3,3,3-trifluoropropene (23)

Hexachloropropene (151 g; 0.61 mol) was fluorinated with antimony trifluoride (72 g; 0.4 mol) at 170 °C, and a mixture of products was collected in a b.p. range 90-115 °C. After treatment of the distillate [15] the main product 23 was obtained by rectification, b.p. 87-91 °C (lit. [17] 88.1 °C), yield 89 g (74.2 %), purity 97 %.

(b) 1,1,2,3-Tetrachloro-3,3-difluoropropene (24) and 1,1,2,3,3-pentachloro-3-fluoropropene (25)

During the fluorination of hexachloropropene, after (a) above, a fraction of b.p. 150-172 °C was collected by means of a rectification dephlegmator. The products 24 and 25 were obtained by rectification after treatment of the distillate: Compound 24, b.p. 126-128 °C (lit. [17] 128.3 °C), compound 25, b.p. 96-100 °C/13.3 kPa (lit. [17] 170 °C).

(c) Chlorination of halogenopropenes 23-25

A mixture of CF_2Cl-$CFCl_2$ (50 ml) and chlorofluoropropene (23-25) was irradiated with an UV lamp (RVK 125 W, Tesla) in an immersion-well reactor at 15-20 °C and dry chlorine gas

was introduced into the mixture. The reaction was stopped at a conversion of 80-90 %. After treatment of the reaction mixture the products 26-28 were isolated by rectification:

Starting compound g (mol)	Product yield g (%)	B.p. °C
CF_3-CCl=CCl_2 (23) 85.5 (0.43)	CF_3-CCl_2-CCl_3 (26) 70 (60)	150-154
CF_2Cl-CCl=CCl_2 (24) 132.5 (0.61)	CF_2Cl-CCl_2-CCl_3 (27) 147 (84)	189-191
$CFCl_2$-CCl=CCl_2 (25) 122 (0.53)	$CFCl_2$-CCl_2-CCl_3 (28) 112 (70)	235-236

Oxygenative dechlorination (i.e. 'hydrolysis') of halogenopropanes 26-28

A mixture of the halogenopropane (26,27 or 28), oleum (60 %) and a catalytic amount of mercuric oxide and silver acetate was heated at 115-125 °C for 8 hours under a reflux condenser. Then a distillate was collected consisting of a mixture of an acid chloride and sulphur trioxide, which was used for the preparation of esters 1,2 and 3, respectively.

(2-Propyl)-pentahalogenopropanoates 1-3

To 2-propanol in a reaction flask crude acid chloride (26,27 or 28) was added dropwise under mixing and cooling (10-15 °C), the mixture was then refluxed 1 hr., cooled, washed with water, then with a concentrated solution of calcium chloride and water, dried with anhydrous magnesium sulphate. The esters 1,2 and 3 were isolated by rectification on a packed column (length 10 cm, ceramic saddles). Ester 1: B.p. 145-147 °C, yield 18.6 (57 %, calcd. to halogenopropane 26), purity 99.5 % (GLC: poly(butanediol succinate), 240 cm). Ester 2: B.p. 160-161 °C, yield 35.1 g (88 %, calcd. to 27), purity 99 %. Ester 3: B.p. 105-106 °C/2.1 kPa, yield 10.2 g (82 % calcd. to 28), purity 99 %.

Methyl 3,3-dichloro-2,3-difluoropropanoate (11)

The compound was prepared according to the described procedure [1] starting with ester 4 (18.7 g, 0.141 mol); the reaction mixture was irradiated 1 hr. and the conversion of the starting compound was monitored by GLC. After the treatment of the reaction mixture, the raw product was distilled and 3 fractions were taken: b.p. 50-53 °C, 53-55 °C, and 55-60 °C, all at pressure 2kPa. The fractions contained changing content of the compounds 11 and 18. The fractions were then re-distilled and 16 fractions were taken with different content of the reduction products 11 and 18, starting with pure product 11 (purity ca. 98 %) and ending with almost pure product 18 (purity 96 %).

Butyl 3-chloro-2,3,3-trifluoropropanoate (12)

The compound was prepared according to the described procedure [1] starting with ester 5 (42.4 g; 0.168 mol). A time dependence of the conversion of the compound 5 was monitored by GLC and the reaction was stopped at the time of total conversion of the compound 5. The product 12 was obtained by rectification, b.p. 97-97.5 °C/6.8 kPa, yield 23.2 g (64.1 %), purity 97.5 % (for GLC see esters 1-3).

Photochemical reduction of butyl 3-chloro-2,3,3-trifluoropropanoate (12)

A mixture of the propanoate 12 (21.3 g; 97.4 mmol) and 2-propanol (250 ml) was irradiated with a UV lamp (RVK 250 W, Tesla) in an immersion-well reactor [1] for 210 hrs. Hydrogen chloride formed was taken off by introducing pure nitrogen. Reaction progress was controlled by GLC. The reaction mixture was poured on ice and the products were taken up with CF_2Cl-$CFCl_2$ (3 x 30 ml). This solution was washed with a concentrated water solution of calcium chloride, water and dried over anhydrous magnesium sulphate, taken down and the Freon was distilled off. The mixture of products was then partly separated by distillation to fractions with b.p. 120 to 150 °C that contained different amounts of the products 14,16,19 and 20.

The fractions were analysed by GLC - Mass spectrometry (for the spectra see Table 4).

General procedure for the photo-reductions

An ester solution in 2-propanol was irradiated in an immersion-well reactor of the content ca. 100 ml with a water-cooled quartz finger containing a medium pressure UV lamp (RVK 250 W, Tesla). A reaction mixture was stirred by introducing pure nitrogen into the mixture. The reaction progress was followed by GLC. After finishing the reaction the mixture was treated as formerly [1].

Kinetic measurements

The reduction reactions were performed with a standardised procedure. A quartz cell of volume 15 ml (round-shaped, 1 cm thick) was filled with a solution of an ester in 2-propanol (0.005 mol/l) and closed with a rubber septum. The solution was deoxygenated by dry nitrogen as formerly [1] (20 and 10 min.), the cell was then placed in a housing and irradiated with focused light of the UV mercury lamp (RVK 250 W, Tesla). Samples for concentration analyses were withdrawn by means of a microsyringe [1].

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