

CHEMISTRY OF ORGANIC FLUORINE COMPOUNDS. X.*
RADICALLY INDUCED REDUCTION OF C—Cl BONDS
IN FLUOROCHLORO DERIVATIVES BY 2-PROPANOL

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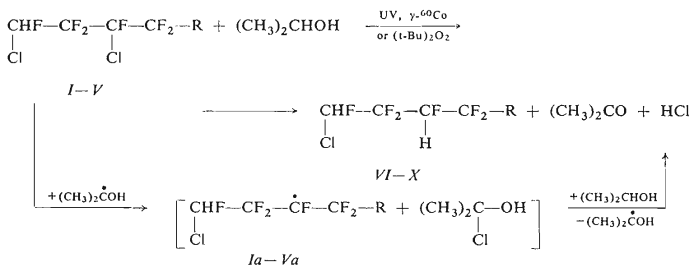
Under the influence of UV or ⁶⁰Co γ -radiation or in the presence of di-tert-butyl peroxide C—Cl bonds in —CClF— groups of fluorochloroalknols of the R¹R²C(OH)(CF₂—CClF)₂—H (*I—IV*) and R¹R²C(OH)(CF₂—CClF)₃—H (*XI, XII*) type, and in fluorochloroalkanones as for example CH₃CO (CF₂—CClF)₂—H (*V*), are selectively reduced in 2-propanol, while the C—Cl bonds in primary —CHClF groups remain intact. 1,1,1-Trifluoro-2,2,2-trichloroethane (*XVII*) and 1,1,1-trifluoro-2,2-dichloroethane (*XVIII*) undergo reduction under these conditions. The course of the reduction and the application of NMR- and IR spectra for the identification of the products are discussed.

The reduction of halo derivatives of alcohols under the conditions of radicalic reaction is mentioned in the literature several times¹⁻⁵, but in the field of fluoro derivatives only the photochemical reduction of the C—I bond in 1,1,2-trifluoro-2-chloro-1-bromo-2-iodoethane with ethanol⁶ was described. In one of the preceding papers of this series⁷ we found that the addition of 2-propanol to trifluorochloroethylene induced by γ -radiation is accompanied by a competitive reduction of the 1 : 2 (*III*) and 1 : 3 (*XII*) telomers, during which C—Cl bonds are reduced only in —CClF-groups, while the C—Cl bond in the terminal —CHClF group remains preserved. We demonstrated⁸ further that the degree of reduction of *III* and *XII* during the addition reaction is influenced by the initial concentrations of trifluorochloroethylene, by temperature, and by the dose of the γ -radiation. In this communication we describe a radically initiated reduction of some fluorochloro derivatives with 2-propanol, which can serve for selective and quantitative reductive splitting off of chlorine atoms inside the chain of telomers under mild conditions⁹.

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We submitted with success the 1 : 2 and 1 : 3 telomers of fluorochloroalkanols or fluorochloroalkanones obtained on addition of trifluorochloroethylene and methanol *I* (ref.^{10,11}), ethanol *II*, *XI* (ref.^{10,12,13}), 2-propanol *III*, *XII* (ref.^{7,8,10,14}), and acetaldehyde *IV*, *V* (ref.^{13,15}), as well as 1,1,1-trifluoro-2,2,2-trichloroethane (*XVII*) and 1,1,1-trifluoro-2,2-dichloroethane (*XVIII*), to reduction with 2-propanol. The reaction was started predominantly by UV radiation, in the case of *III* and *XII* γ -radiation ⁶⁰Co (2.3–10²⁰ eV/ml) or di-tert-butyl peroxide were applied as well. Fluorochloroethanes *XVII*, *XVIII* were reduced with 2-propanol on initiation by γ -radiation only. Most satisfactory results were achieved on photochemically induced reaction of fluorochloro derivative in an approximately 20-fold molar excess of 2-propanol, when the reduction took place as a rule quantitatively (Table I). On reduction of 1 : 2 telomers we obtained from 2,2,3,4,4,5-hexafluoro-3,5-dichloropentanol^{10,11} (*I*) 2,2,3,4,4,5-hexafluoro-5-chloropentanol (*VI*), and from 3,3,4,5,5,6-hexafluoro-4,6-dichloro-2-hexanol^{10,12,13} (*II*) 3,3,4,5,5,6-hexafluoro-6-chloro-2-hexanol (*VII*). 2-Methyl-3,3,4,5,5,6-hexafluoro-4,6-dichloro-2-hexanol^{7,8,10,14} (*III*) gave with all three methods of initiation 2-methyl-3,3,4,5,5,6-hexafluoro-6-chloro-2-hexanol (*VIII*)⁷. On photochemical reduction of 3-methyl-1,2,2,4,4,5,6,7-nonafluoro-1,5,7-trichloro-3-heptanol^{13,15} (*IV*) with 2-propanol a mixture of diastereomeric racemates of 3-methyl-1,2,2,4,4,5,6,6,7-nonafluoro-1,7-dichloro-3-heptanol (*IX*) was obtained, which on gas chromatographic analysis gave 2 peaks in a 1 : 1 ratio. Among fluorochloroalkanones was photochemically reduced with 2-propanol 3,3,4,5,5,6-hexafluoro-4,6-dichloro-2-hexanone^{13,15} (*V*), giving 3,3,4,5,5,6-hexafluoro-6-chloro-2-hexanone (*X*). For the sake of comparison the same ketone (*X*) was also prepared by oxidation of alcohol *VII* with chromium trioxide. 1 : 3 Telomeric fluorochloroalkanols *XI*, *XII* contain in their chain two —CClF—groups which may undergo reduction. After photochemical reduction of 3,3,4,5,5,6,7,7,8-nonafluoro-4,6,8-trichloro-2-octanol^{10,12,13} (*XI*) with 2-propanol we isolated only the product of reduction of both —CClF—groups, *i.e.* 3,3,4,5,5,6,7,7,8-nonafluoro-8-chloro-2-octanol (*XVI*)⁷. However, when 2-methyl-3,3,4,5,5,6,7,7,8-nonafluoro-4,6,8-trichloro-2-octanol^{7,8,10,14} (*XII*) was reduced after initiation with γ -radiation or di-tert-butyl peroxide, we isolated both the product of partial reduction, to which we assign on the basis of its NMR-spectrum the structure of 2-methyl-3,3,4,5,5,6,7,7,8-nonafluoro-4,8-dichloro-2-octanol^{7,8} (*XIII*), and the product of total reduction, *i.e.* 2-methyl-3,3,4,5,5,6,7,7,8-nonafluoro-8-chloro-2-octanol^{7,8} (*XV*), as well.

Radically induced reduction with 2-propanol takes place also with simpler fluorochloro derivatives. After irradiation of a solution of 1,1,1-trifluoro-2,2,2-trichloroethane (*XVII*) with ⁶⁰Co γ -radiation we identified in the reaction mixture on the basis of comparison with a standard¹⁶ and gas chromatographical analysis 1,1,1-trifluoro-2,2-dichloroethane (*XVIII*). Further reduction of *XVIII* to 1,1,1-trifluoro-2-chloroethane (*XIX*) takes place as well, but less easily (Eq. A and Table I). Recently this method was also used for the reduction of fluorochloropropanes¹⁷.



In formulae *I, VI*: R = CH₂OH; *II, VII*: R = CH₃CH(OH); *III, VIII*: R = (CH₃)₂C(OH)
IV, IX: R = CH₃C(OH)CF₂CHClF; *V, X*: R = CH₃CO

SCHEME 1

During the reduction of fluorochloro derivatives 2-propanol is oxidized to acetone and the latter may serve together with the resultant hydrogen chloride as a measure of the degree of reduction (Eq. (A), Scheme 1 and 2). Using quantitative chromatographic analysis and the titration of the reaction mixture after reduction of alcohol *III*, initiated by γ -radiation, we found that the yield of acetone and hydrogen chloride corresponds satisfactorily to the expected, stoichiometric value. We showed then by a control experiment that during the radiolysis of 2-propanol alone, using a 2.3 to 10²⁰ eV/ml dose of ⁶⁰Co γ -radiation, acetone is absent among the reaction products; however, higher-boiling fractions of this reaction^{18,19} have not been investigated.

The fact that the radically induced reduction of fluorochloroalkanol with 2-propanol takes place selectively on —CClF-groups and that the reduction of the chlorine atom in the terminal —CHClF group does not take place was corroborated by experiments with 2-methyl-3,3,4-trifluoro-4-chloro-2-butanol^{7,8,10,14} (*XX*), reduced 1 : 2 telomer *VIII*, and reduced 1 : 3 telomer *XV* (Table 1). In these cases we regenerated practically quantitatively the starting alcohols *VIII*, *XV*, and *XX*, and we were unable to prove either acetone or chloride ions in the reaction mixture in sufficient amounts.

We base our considerations on the fact that the reduction of fluorochloro derivatives with 2-propanol takes place by a radical mechanism¹⁻⁶. We assume that the dominant initial step of the reduction is the formation of 2-hydroxy-2-propyl radical by an interaction of 2-propanol with ultraviolet or ionising radiation, or by an interaction with tert-butyl radicals²⁰ formed on fragmentation of the organic initiator. C—Cl bonds in —CClF-groups are cleaved primarily by an attack of the 2-hydroxy-2-propyl radical on the molecules of fluorochloro derivative, leading to radicals *Ia-Va*, acetone, and hydrochloric acid (Scheme 1); this is because the stability and

TABLE I
Conditions and the Results of the Reduction of Fluorochloro Derivatives with 2-Propanol

Fluorochloro derivative g	2-Propanol, g initiation ^a	Time, h (temp., °C)	Product % ^b (g)
<i>I</i> 4·5	11 <i>A</i>	11 (25)	<i>VI</i> 100 (2·8)
<i>II</i> 5·55	29 <i>A</i>	20 (25)	<i>VII</i> 100 (4·5)
<i>II</i> 1·9	1·6 <i>A</i>	^c (25)	<i>VII</i> 64
<i>II</i> 4·7	13 <i>A</i>	14 (25)	<i>VII</i> 100
<i>II</i> 2·8	— <i>A</i>	21 (25)	^d
<i>III</i> 32·9	26 <i>A</i>	16 (25)	<i>VIII</i> 47
<i>III</i> 32·9	26 <i>A</i>	27 (25)	<i>VIII</i> 52
<i>III</i> 8·35	19·1 <i>A</i>	15 (25)	<i>VIII</i> 100
<i>III</i> 0·82	0·88 <i>B</i>	^c (25)	<i>VIII</i> 28
<i>III</i> 1·65	1·95 <i>C</i>	8 (130)	<i>VIII</i> 92
<i>IV + XI</i> 10·1	66 <i>A</i>	31 (25)	<i>IX + XVI</i> 100 100 (5·8)
<i>V</i> 3·1	12·7 <i>A</i>	26 (25)	<i>X</i> 90
<i>XI</i> 2·0	20 <i>A</i>	7 (25)	<i>XVI</i> 100 (1·06)
<i>XII</i> 0·80	1·0 <i>B</i>	^c (25)	<i>XIII + XV</i> 79 6

TABLE I
(Continued)

Fluorochloro derivative g	2-Propanol, g initiation ^a	Time, h (temp., °C)	Product % ^b (g)
<i>XII</i> 1.45	2.0 <i>C</i>	8 (130)	<i>XIII</i> + <i>XV</i> 38 59
<i>XVII</i> 1.05	0.75 <i>B</i>	^c (25)	<i>XVIII</i> 33
<i>XVIII</i> 1.2	0.6 <i>B</i>	^c (25)	<i>XIX</i> 12
<i>XX</i> 0.55	1.0 <i>B</i>	^c (25)	^d
<i>XX</i> 1.9	1.45 <i>C</i>	8 (130)	^d
<i>VIII</i> 1.7	1.8 <i>C</i>	8 (140)	^d
<i>XV</i> 1.62	2.05 <i>C</i>	8 (130)	^d

^a *A* UV radiation, *B* γ -⁶⁰Co radiation, *C* di-tert-butyl peroxide, 40–50 weight percent of fluoro-chloro derivative; ^b weight percents determined from chromatograms; ^c total dose $2.8 \cdot 10^{22}$ eV of γ -radiation; ^d does not react.

—CHF-group proton at $4.41-4.49\tau$ in the form of a doublet of multiplets, and also a change in the chemical shift of the proton signals both of the primary —CHClF-group and the H—C—O and methyl groups. This is a consequence of the substitution of the electronegative chlorine atom by hydrogen, which causes an increase in the shielding of the nuclei of hydrogen atoms on β -carbon atoms (with respect to the —CHClF-group); this is manifested by a signal shifted upfield. In the case of —CHClF-groups in compounds *VI-X*, *XV* and *XVI* this increase is $\sim 0.3\tau$. Thus, the values are close to those of the proton signal of the same group in the 1 : 1 adduct *XX*. In the H—C—O group in compounds *VI*, *VII*, and *XVI* the signal shift is also $\sim 0.3\tau$. The shielding effect decreases with the distance and makes itself weakly visible by the change of the chemical shift of methyl groups by $0.04-0.09\tau$ also on γ -carbon atoms (with respect to the —CHF-group) in compounds *VII-X*, *XV*,

TABLE II
 Constants and Analyses of the Reduction Products VI, VII, IX, and X

Product (M.w.)	B.p., °C/Torr	Calculated/Found				IR spectrum ^a
		% C	% H	% Cl	% F	
VI C ₅ H ₅ ClF ₆ O (230.5)	72—73/18	26.05	2.19	15.38	49.45	825 ms, 835 ms, 846 ms, 878 ms, 932 ms, 1035 ms, 1080 vs, 1120 s, 1185 vs, 1237 s, 1345 w, 1355 ms, 1381 ms, 1456 w, 1555 w, 2895 ms, 2958 s, 2989 ms, 3400 vs, 3635 vs
		26.60	2.37	15.19	49.58	
VII C ₆ H ₇ ClF ₆ O (244.6)	87—90/20	29.46	2.88	14.49	46.62	821 ms, 834 ms, 869 ms, 879 sh, ms, 910 w, 1010 ms, 1030 ms, 1080 vs, 1118 vs, 1128 sh, ws, 1177 s, 1200 s, 1238 s, 1254 sh, vs, 1283 sh, ms, 1335 sh, w, 1350 w, 1384 ms, 1457 w, 1553 w, 2850 sh, w, 2900 ms, 2953 s, 3000 s, 3420 vs, 3618 s
		29.84	3.10	14.97	46.71	
IX C ₈ H ₇ Cl ₂ F ₉ O (361.0)	115—120/24	26.61	1.96	19.64	47.36	831 ms, 845 sh, ms, 853 ms, 872 ms, 938 w, 1038 s, 1082 vs, 1148 vs, 1178 sh, s, 1206 s, 1232 s, 1258 s, 1287 ms, 1355 ms, 1387 ms, 1398 ms, 1468 w, 1610 w, 2850 w, 2900 sh, ms, 2930 ms, 2970 sh, ms, 3020 ms, 3480 s, 3570 sh, s, 3605 vs, 3680 ms
		27.03	2.16	19.41	46.25	
X C ₆ H ₅ ClF ₆ O (242.6)	145—150	29.71	2.08	14.61	47.00	819 ms, 847 ms, 868 s, 876 sh, ms, 940 w, 961 w, 1008 ms, 1040 sh, ms, 1053 s, 1083 vs, 1112 vs, 1130 vs, 1112 vs, 1130 vs, 1142 sh, vs, 1204 vs, 1231 s, 1252 s, 1268 s, 1294 sh, vs, 1350 sh, ms, 1371 s, 1390 sh, ms, 1768 vs, 2850 w, 2935 ms, 2995 ms, 3021 ms, 3490 ms
		30.02	2.14	14.92	47.14	

^a For 800—2000 cm⁻¹ measured in tetrachloromethane, for 2600—3700 cm⁻¹ liquid sample was measured.

and XVI. These facts corroborate our earlier assumption⁸ regarding the structure of partially reduced fluorochloroalkanol formed from the 1 : 3 telomer XII; the assumption was based on the considerations regarding the stability and the ease of formation of the intermediary radical. As the PMR spectrum of this partially

TABLE III
PMR Spectra of Starting Fluorochloro Derivatives I—V, XI, XII, and XX

Values of ^{a,b}	I ^c		II	III ^c		IV		V ^c		XI ^c		XII	XX
H—CFCl	3.42 (2 m)	3.47 (2 m)	3.39 (2 m)	3.29 (2 m)	3.35	3.25 3.72	3.41 (2 m)	3.48	3.41 (2 t)	3.40 (2 dd)	3.44 (2 m)	3.57 (2 m)	
² J _{HF}	47.0	46.6	47.0	48.4	47.9	45.0	47.0	46.9	47.0	47.0	48.0	47.7	
³ J _{HF}	13.1 2.1	12.7 3.0	—	14.0 1.6	3.6 2.0	—	13.7 1.6	13.3 2.4	12.5 12.5	10.0 13.0	—	14.5 1.6	
H—C—O	5.91 (t; J = 14.5)		5.56 (m)	—	—	—	—	—	5.58 (m)	—	—	—	—
CH ₃	—		8.60 (d) J = 7.0	8.54 (bs)	8.24 (bs)	7.56 (bs)	7.55 (bs)	8.61 (bd)	8.59 (bs)	8.62 (bs)			
OH	6.39 (s)		7.25 (s)	7.85 (s)	7.00 (s)	—	7.08 (bs)	7.56 (s)	7.36 (s)				

^a Values of chemical shifts in τ ; ^b Values of coupling constants in Hz; ^c Values of chemical shifts and coupling constants are given for single diastereomeric racemates, in other instances average values are given only.

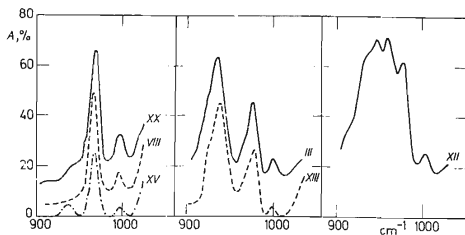


FIG. 1
IR Spectra (900—1040 cm^{-1}) of Fluorochloroalkanols III, VIII, XII, XIII, XV, and XX
The position of the absorption bands is lowered in comparison with the fundamental scale by 10% (alcohol VIII) and by 20% (alcohol XV, XIII).

TABLE IV
PMR Spectra of the Reduction Products of VI—X, XIII, XV, and XVI

Value of ^{a,b}	VI	VII	VIII	IX	X	XIII	XV	XVI
H—CFCl	3.75 (2 m)	3.70 (2 m)	3.66 (2 m)	3.54 3.58 3.70	3.74 (2 m)	3.70 (2 m)	3.71	3.69 (2 bt)
² J _{HF}	47.0 43 ^c	48.0 44 ^c	48.0 43 ^c	47.0 48.0 42 ^c	48.5 43 ^c	48.0 43 ^c	48.0 43 ^c	48.0 42 ^c
³ J _{HF}	7.0 7.0	7.5	7.0 7.0	12.5 10 13	—	—	7.5	—
H—CF	4.94 (2 m)	4.85 (2 m)	4.65 (2 m)	4.70 (2 m)	4.69 (2 m)	4.41 (2 m)	4.83	4.84 (2 m)
H—C—O	6.15 (t) J = 12.0	5.95 (m)	—	—	—	—	—	5.89 (m)
CH ₃	—	8.67 (d) J = 6.0	8.63 (bs)	8.39 (bs)	7.60	8.55 (bs)	8.68 (bs)	8.67 (d) J = 6.0
OH	6.36 (s)	6.85 (s)	7.76 (s)	6.81 (bs)	—	7.48 (s)	7.68 (s)	6.80 (bs)

^{a,b} See footnotes of the Table III; ^c value for —CFH—.

reduced fluorochloroalkanol shows certain differences when compared with the spectrum of XII, as for example the shifts of protons in the —CHClF-group (0.26 τ) and in the methyl groups (0.04 τ), it can be assumed that the —CHF-group is in β -position with respect to the —CHClF group. These assumptions agree with the structure XIII but not with XIV (Scheme 2). In addition to this the signal of the —CHF-proton has the lowest value (4.41 τ) which is in full agreement with the effect of two chlorine atoms on carbons in both β and β' positions.

The comparison of the IR spectra of fluorochloroalkanols III, XII, and XX obtained on addition of 2-propanol to trifluorochloroethylene^{8,10,14} with the IR spectra of their reduction products VIII, XIII, and XV is also remarkable (Fig. 1). In the finger-print region (900–1040 cm⁻¹) the number of C—Cl bonds in the molecule

influences the complexity and the shape of the spectrum, so that in this region alcohols *VIII*, *XV*, and *XX* which contain a sole chlorine atom in the terminal —CHClF group have an identical form and position of the absorption maxima as alcohols *III* and *XIII* in which in addition to the chlorine atom in the mentioned terminal group, another chlorine atom in the —CClF-group is present.

EXPERIMENTAL

Temperature data are not corrected. Gas chromatographical analyses were carried out on a Griffin & George apparatus, Mk II B, TC-detection, and on a Chrom II chromatograph with FID. Preparative gas chromatography was carried out on an apparatus of non-commercial origin²². Unless stated otherwise Celite 545 was taken as the support of the stationary phase. Poly(propylene sebacate) served as the stationary phase and nitrogen as the carrier gas. The IR spectra were measured on a UR 10 C Zeiss (Jena) spectrophotometer, the NMR spectra on a Tesla BS 487 A (80 MHz) apparatus, both in tetrachloromethane.

Reduction of Fluorochloro Derivatives with 2-Propanol

A) *Initiated by UV radiation*: A solution of fluorochloro derivative in approx. a 20-molar excess of 2-propanol in a quartz test tube was irradiated by a high-pressure mercury lamp of 400 W at 25°C. The course of the reduction was followed by gas chromatographical analysis and when the conversion was 100% the excess 2-propanol was distilled off and the residue rectified or worked up by preparative gas chromatography. The conditions and the results are presented in Table I, the constants of the as yet undescribed compounds are listed in Table II, and the NMR spectra are in Tables III and IV.

B) *Initiated by γ -radiation* ⁶⁰Co: Into a glass ampoule (approx. 2 ml) a mixture (1.5 ml) of fluorochloro derivative and 2-propanol was placed and the ampoule was rinsed with nitrogen, sealed, and irradiated by a total dose of $2.8 \cdot 10^{22}$ eV of γ -radiation ⁶⁰Co. After this the ampoule was opened and its content analysed by gas chromatography at 182–196°C. The amount of the formed acetone was also determined by gas chromatography, taking a sample of the reaction products for analysis. The analysis was carried out at 68°C using a column filled with 20% polyethylene glycol 444 on Celite. The products were identified by comparison with authentic samples prepared earlier^{7,8,10–15}. The conditions and the results are given in Table I.

C) *Initiated by di-tert-butyl peroxide*: A glass ampoule (approx. 5 ml) was filled with a mixture of the fluorochloro derivative, 2-propanol, and di-tert-butyl peroxide (40–50% of the weight of the fluorochloro derivative). The ampoule was rinsed with nitrogen, sealed and heated at 140–150°C for 8 hours. It was then opened and the contents was analysed by gas chromatography at 188°C, using the method of internal standards and comparison with authentic samples^{7,8,10–15}. The conditions and the results are given in Table I.

3,3,4,5,5,6-Hexafluoro-6-chloro-2-hexanone (*X*)

4.1 g (0.016 mol) of alcohol *VII* were mixed with a solution of 5.3 g (0.018 mol) of potassium dichromate, 2.4 ml of conc. sulfuric acid, and 25 ml of water, and the mixture was stirred under reflux for 20 hours. The reaction mixture was extracted with ether and the extract was neutralized, dried with ether, and evaporated. Distillation of the residue gave 2.3 g (0.009 mol, 56.35%) of ketone *X*, b.p. 145–150°C. According to IR spectra and gas chromatography ketone *X* was identical with the ketone obtained on photochemical reduction of ketone *V* with 2-propanol (Table I).

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