# RADICAL REDUCTION OF C–Cl BONDS IN CHLOROFLUORO ETHERS

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Reduction of C–Cl bonds in 2,2-dichloro-1,1,2-trifluoroethyl trichloromethyl ether (*I*), 2-chloro-1,1,2-trifluoroethyl trichloromethyl ether (*II*), and 2,2-dichloro-1,1,2-trifluoroethyl dichloromethyl ether (*III*) with 2-propanol, 2-butanol, cyclohexanol, tetrahydrofuran, diethyl ether, and 1,3-dioxolane initiated photochemically and by radiation has been investigated. Beside the main reduction products – 2-chloro-1,1,2-trifluoroethyl dichloromethyl ether (*IV*) and 2-chloro-1,1,2-trifluoroethyl chloromethyl ether (*V*) – it was also possible to prove the formation of 1,2-dichloro-1,2-bis(2-chloro-1,1,2-trifluoroethoxy)ethane (*VI*), 1-chloro-1,2-bis(2-chloro-1,1,2-trifluoroethoxy)ethene (*VII*), and 1,2-dichloro-1,2-bis(2-chloro-1,1,2-trifluoroethoxy)ethene (*VIII*). The structure of products was confirmed by elemental analysis, MS, IR, $^1$H NMR and $^{19}$F NMR spectra and by GLC comparison of the elution times with those of the standards. The relative reduction ability of the solvents used and the reduction rate order of C–Cl bonds in the compounds ($CCl_3$ > $CFCl_2$ > $CHCl_2$ and CFClH) are given.

Dědek and Liška[1 – 3] studied the addition of 2-propanol to chlorotrifluoroethylene initiated photochemically and by radiation and observed formation of the products formed from the primary 1 : 2 and 1 : 3 telomers by chemoselective reduction of C–Cl bonds in CFCl groups by action of 2-propanol under radical conditions. No reduction took place in the terminal HCFCl group. In an independent way they confirmed this reduction in other chlorofluoro compounds by action of 2-propanol, tetrahydrofuran, and 1,3-dioxolane initiated by UV and γ-$^{60}$Co radiation. The radical mechanism of photochemically induced reduction of C–Cl bonds with 2-propanol was proved e.g. in 1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane[4] (DDT) and in various fluorohalo compounds[5].

In the present work we have investigated the reduction of C–Cl bonds in $CCl_3$, $CHCl_2$, and $CFCl_2$ groups of 2,2-dichloro-1,1,2-trifluoroethyl trichloromethyl ether (*I*), 2-chloro-1,1,2-trifluoroethyl trichloromethyl ether (*II*), and 2,2-dichloro-1,1,2-trifluoroethyl dichloromethyl ether (*III*) with the aim of preparation of 2-chloro-1,1,2-trifluoroethyl dichloromethyl ether (*IV*) which is an intermediate in the production of 2-chloro-1,1,2-trifluoroethyl difluoromethyl ether – the inhalation anaesthetic enfluran[6].

$CFCl_2-CF_2-O-CCl_3$ $HCFCl-CF_2-O-CCl_3$ $CFCl_2-CF_2-O-CHCl_2$

*I* *II* *III*

$HCFCl-CF_2-O-CHCl_2$

*IV*

The reduction agents used included alcohols (ethanol, 2-propanol, 2-butanol, 3-pentanol, cyclohexanol) and ethers (tetrahydrofuran, 1,3-dioxolane, and diethyl ether). We investigated the reduction abilities of the solvents used and the effect of molar ratio of the solvent to the chlorinated ether upon the rate and degree of reduction of C–Cl bonds. The experimental conditions of the reductions are presented in Table I. The reaction course was monitored by gas chromatography, and the time dependences of relative proportions of halo ethers in the reaction mixture are given graphically.

The photochemically induced reduction of ether *II* with 2-propanol was found to proceed chemoselectively in the $CCl_3$ group to give ether *IV*. Only after complete conversion of ether *II* into ether *IV* there begins the reduction of C–Cl bonds in the $CHCl_2$ group of the ether *IV* formed to give ether *V* (see Fig. 1, Table I, experiment No. 1). Under the same conditions, the C–Cl bonds in $CFCl_2$ group of ether *III* are reduced with high selectivity; at first ether *IV* is formed predominantly, and then it is reduced to

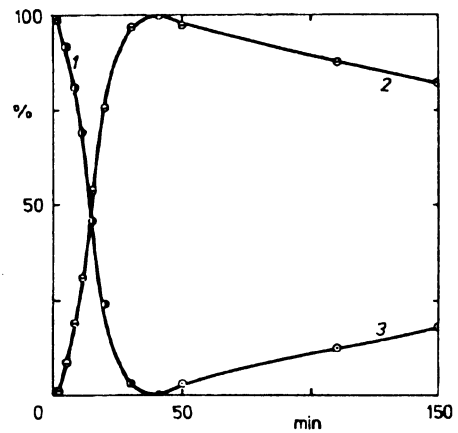


FIG. 1

Relative proportions of halo ethers in the reaction mixture during photochemically induced reduction of ether *II* with 2-propanol (experiment No. 1). *1* ether *II*, *2* ether *IV*, *3* ether *V*

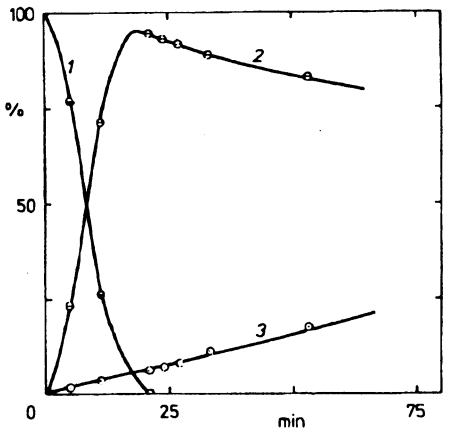


FIG. 2

Relative proportions of halo ethers in the reaction mixture during photochemically induced reduction of ether *III* with 2-propanol (experiment No. 2). *1* ether *III*, *2* ether *IV*, *3* ether *V*

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TABLE I

Experimental conditions of photochemically induced reductions of C–Cl bonds in ethers *I* – *IV* and their mixtures by alcohols and ethers. Mr means rounded off molar ratio of reducing agent to reduced substrate; *V* total volume of reaction mixture; *t* temperature at the surface of reactor +/– 3 °C

| Experiment No. | Educt, g/ml/mol | | Reducing agent[a], g/ml/mol | | Mr | *V*, ml | *t*, °C | τ, min | Fig. |
|---|---|---|---|---|---|---|---|---|---|
| 1 | *II* | 29.9/18/0.115 | 2P | 73/92/1.215 | 10 | 110 | 30 | 150 | 1 |
| 2 | *III* | 29.3/18/0.116 | 2P | 73/92/1.215 | 10 | 110 | 30 | 53 | 2, 3 |
| 3 | *I* | 34.2/20/0.119 | 2P | 71/90/1.1183 | 10 | 100 | 30 | 150 | 3 |
| 4 | *I* | 56.4/33/0.200 | 2P | 59/75/0.982 | 5 | 100 | 30 | 370 | |
| 5 | *I* | 29.1/17/0.102 | 2B | 75.3/93/1.017 | 10 | 110 | 30 | 155 | 3 |
| 6 | *I* | 23.9/14/0.084 | 3P | 78.8/96/0.836 | 10 | 110 | 30 | 135 | 3 |
| 7 | *I* | 25.7/15/0.090 | CH | 91.2/95/0.910 | 10 | 110 | 45 | 220 | 3 |
| 8 | *I* | 27.4/16/0.096 | ET | 66.2/84/1.439 | 15 | 100 | 30 | 135 | 3 |
| 9 | *I* | 32.5/19/0.114 | DOX | 97.0/91/1.309 | 10 | 110 | 30 | 240 | 4 |
| 10 | *I* | 32.5/19/0.115 | THF | 81/91/1.123 | 10 | 110 | 30 | 135 | 4 |
| 11 | *I* | 25.7/15/0.090 | DEE | 67.5/95/0.910 | 10 | 110 | 25 | 165 | 4 |
| 12 | A[b] | 32/20/X | 2P | 70.2/90/1.17 | X | 110 | 30 | 45 | 5 |
| 13 | *IV* | 26.5/17/0.122 | 2P | 72.5/93/1.207 | 10 | 100 | 30 | 150 | |
| 14 | *II* | 30.0/18/0.119 | 2P | 71.8/92/1.194 | 10 | 110 | 30 | 145 | |

[a] 2P, 2-propanol; 3P, 3-pentanol; 2B, 2-butanol; CH, cyclohexanol; ET, ethanol; DOX, 1,3-dioxolane; THF, tetrahydrofuran; DEE, diethyl ether. [b] Mixture of 2% *I*, 62% *II*, 32% *III*, 4% *IV*.

ether *V* (Fig. 2, experiment No. 2, Table I). The reduction course observed indicates distinct differences between reactivities of the individual C–Cl bonds which decrease in the order $CCl_3$ > $CFCl_2$ > $CHCl_2$ >>> CFClH.

$$HCFCl-CF_2-O-CH_2Cl$$

*V*

The observed different reactivities of C–Cl bonds in the groups given can be practically utilized for transformations of ethers *I* – *III* into ether *IV*. Ethers *I* – *III* are always formed as side products in the production of ether *IV* by chlorination of 2-chloro-1,1,2-trifluoroethyl methyl ether and must be separated by a high-performance rectification.

The photochemically induced reduction of C–Cl bonds in ether *I* was studied in more detail. It was found that the reduction with 2-propanol proceeds in accordance with the above-mentioned reactivity order of C–Cl bonds in the individual groups. At first the chlorine in $CCl_3$ group is reductively removed to give ether *III* which is subsequently reduced in its $CFCl_2$ group to give ether *IV*. The reduction of chlorine substituent in $CHCl_2$ group is the most difficult one, and the conversion of ether *IV* into ether *V* is slow. Both the reduction rate and the conversion degree are affected by molar ratio of 2-propanol to ether *I*; if this ratio was 10 : 1, the reduction of ether *I* gave a mixture of ethers *IV* and *V* in the ratio of 96 : 4. With a 5 : 1 excess the reduction is slow and practically stops after the first step; the ratio of produced ethers is *III* : *IV* = 92 : 8.

Further experiments were focused on the reduction efficiency of the alcohols and ethers. The time decrease in the relative content of ether *I* (Fig. 3) shows the following order of reduction ability of alcohols: 2-propanol > 2-butanol > cyclohexanol > ethanol

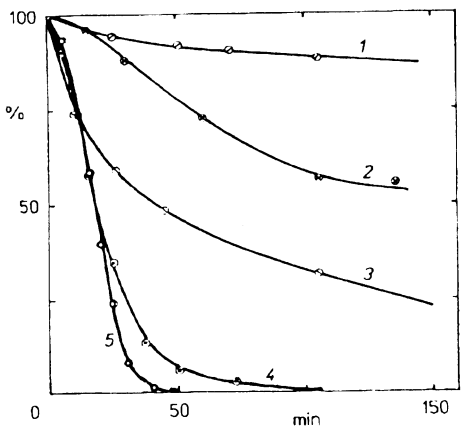



FIG. 3
Comparison of reduction abilities of alcohols used in photochemically induced reductions of ether *I*. Relative proportion of starting ether *I* in reaction mixture (experiments Nos 3, 5 – 8). *1* 3-pentanol, *2* ethanol, *3* cyclohexanol, *4* 2-butanol, *5* 2-propanol

> 3-pentanol. Analogous time dependences (Fig. 4) show the following reduction abilities of ethers: tetrahydrofuran > 1,3-dioxolane and diethyl ether.

From the standpoint of preparative transformation of ether *I* into ether *IV* (with transient formation of ether *III*) the most advantageous reducing agent is 2-propanol. The different reduction rates of C–Cl bonds in ethers *I* – *IV* can be utilized in the process of production of ether *IV* (ref.[7]) which is obtained by chlorination of 2-chloro-1,1,2-trifluoroethyl methyl ether (*XVI*). Its chlorination gives ethers *I* – *III* as side products which accumulate in the distillation residues after rectification of the main portion of ether *IV*. Such a mixture of ethers *I* – *IV* was transformed into the required ether *IV* (with an admixture of ether *V*) by a photochemically induced reduction with 2-propanol, which is represented in Fig. 5 giving the time dependences of relative content of ethers *I* – *V* during the reduction.

The reduction of ether *I* with a tenfold molar excess of 2-propanol was also carried out with the initiation with γ radiation of $^{60}Co$. It was found that the reduction of chlorine substituent took place only in the $CCl_3$ group of ether *I* to give ether *III*, the dose used being as little as 60 kGy. The reduction of ether *III* into the required ether *IV* did not take place, not even with application of higher radiation doses (up to 250 kGy).

The distillation residues after rectification of the reaction mixture from photochemically induced reduction of ether *I* with 2-propanol contained 1,2-dichloro-1,2-bis(2-chloro-1,1,2-trifluoroethoxy)ethane (*VI*), 1-chloro-1,2-bis(2-chloro-1,1,2-trifluoroethoxy)-

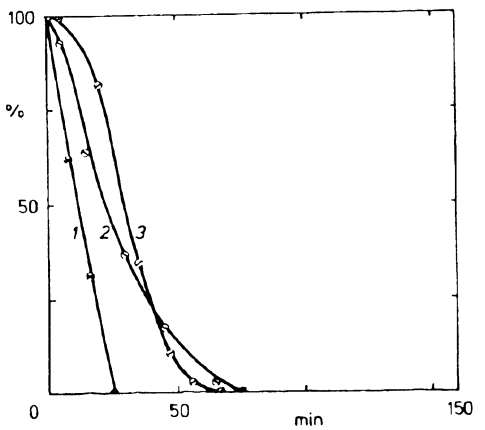



Fig. 4

Comparison of reduction abilities of ethers used in photochemically induced reductions of ether *I*. Relative proportion of starting ether *I* in reaction mixture (experiments Nos 9 – 11). *1* tetrahydrofuran, *2* 1,3-dioxolane, *3* diethyl ether

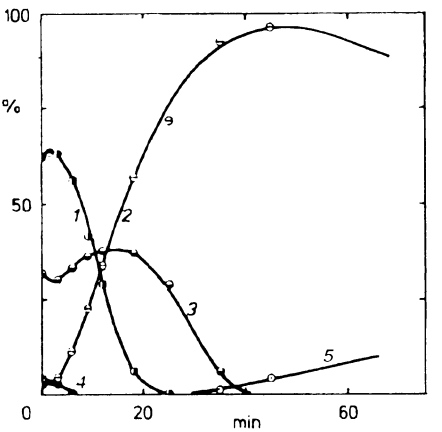
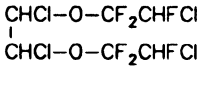


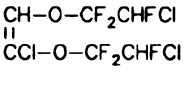

Fig. 5

Relative proportions of halo ethers in reaction mixture during photochemically induced reduction of mixture of ethers *I* – *V* (mixture A) with 2-propanol (experiment No. 12). *1* ether *II*, *2* ether *IV*, *3* ether *III*, *4* ether *I*, *5* ether *V*

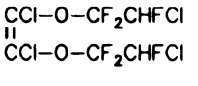
ethene (*VII*), 1,2-dichloro-1,2-bis(2-chloro-1,1,2-trifluoroethoxy)ethene (*VIII*), and 3,6-dichloro-5,5,6-trifluoro-2-methyl-4-oxa-2-hexanol (*IX*).



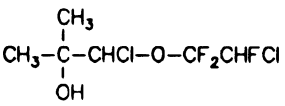
*VI*



*VII*

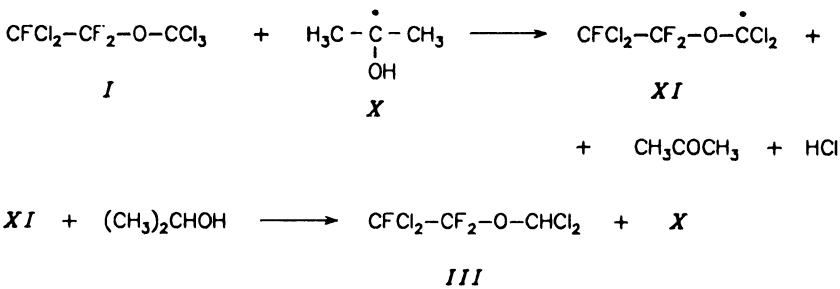


*VIII*



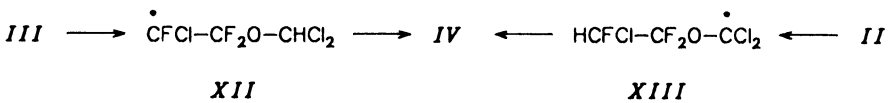
*IX*

The photochemical reduction of C–Cl bonds is interpreted by a radical mechanism[4]. It is presumed that at first the C–Cl bond of trichloromethyl group of ether *I* is split by photolysis or by action of the ketyl radical *X* to give the radical *XI* which produces ether *III* and ketyl radical *X* by the chain transfer to 2-propanol. Acetone was always detected in the reaction products (Scheme 1).



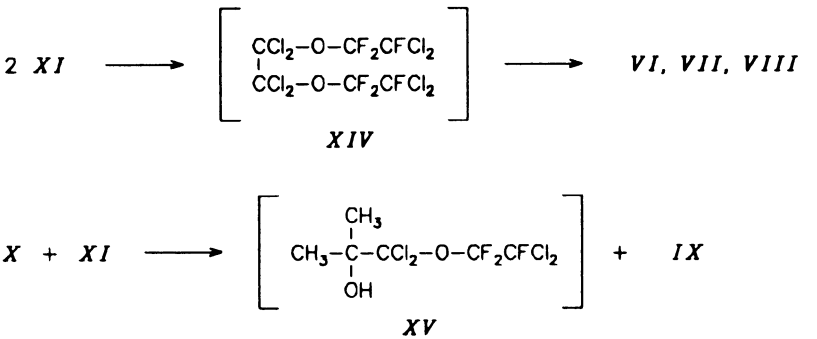
SCHEME 1

Similarly it is possible to explain the formation of ether *IV* from ether *III* via the radical intermediate *XII* or from ether *II* via the radical intermediate *XIII* (Scheme 2).



SCHEME 2

Also the formation of compounds *VI* – *IX* has its origin in reactions of transient radical intermediates: it is presumed that dimeration of radical *XI* gives the dimer *XIV*, recombination of radical *X* with *XI* produces alcohol *XV*. Under the conditions given, the compounds *XIV* and *XV* are reduced to ethers *VI* – *VIII* and alcohol *IX*, respectively (Scheme 3).




SCHEME 3

## EXPERIMENTAL

The temperature data were not corrected. The $^1H$ and $^{19}F$ NMR spectra were measured in deuteriochloroform with a Varian XL 100 apparatus using tetramethylsilane and fluorotrichloromethane, respectively, as the internal standards. The chemical shifts are given in ppm, the coupling constants $J$ in Hz. The IR spectra ($\tilde{\nu}$, $cm^{-1}$) were measured (if not otherwise stated) in carbon disulfide with a Perkin–Elmer 225 apparatus. The mass spectra were measured with a Gas-Chromatograph-Mass-Spectrometer LKB 9000. The GLC analyses were carried out on a Chrom 5 apparatus.

### 2-Chloro-1,1,2-trifluoroethyl Methyl Ether (*XVI*)

The ether *XVI* was prepared by a reaction of chlorotrifluoroethylene with a methanolic solution of potassium hydroxide[8] at 50 °C; b.p. 69.5 – 70.5 °C, $\rho$ 1.36 g $cm^{-3}$ (ref.[8] gives b.p. 64.4 °C/83.98 kPa, $\rho$ 1.3632 g $cm^{-3}$).

### 2,2-Dichloro-1,1,2-trifluoroethyl Trichloromethyl Ether[9] (*I*)

A photochemical quartz reactor of 1 000 ml volume was charged with 950 g (700 ml, 6.41 mol) methyl ether *XVI*. The reactor was equipped with a high-pressure discharge lamp 125 W, a reflux condenser with condensation trap filled with solid carbon dioxide and ethanol, and a through-flow absorber of the hydrogen chloride set free. Chlorine was introduced into the reactor and the reaction course was monitored chromatographically (SE 301, 150 °C, 0.105 MPa, $N_2$). After the total conversion of the educt, the reaction mixture was washed with water, saturated solution of sodium sulfite, saturated solution of potassium hydrogen carbonate, dried with anhydrous calcium chloride, and distilled. Yield 1 430 g ether *I* (78%), b.p. 149 – 151 °C, $\rho$ 1.71 g $cm^{-3}$ (ref.[10] gives b.p. 142 °C/83.44 kPa, $\rho$ 1.7141 g $cm^{-3}$). For $C_3Cl_5F_3O$ (286.2) calculated: 12.52% C, 61.92% Cl, 19.91% F; found: 12.42% C, 61.53% Cl, 19.41% F. MS, *m/z* (rel. int., %): 152 (65), 150 (100), 119 (38), 117 (41), 102 (25), 101 (39), 65 (17), 63 (52), 47 (17), 31 (20). $^{19}F$ NMR

spectrum: 76.37 t, 1 F ($CFCl_2$, $^3J$(F,F) = 10), 86.77 m, 2 F, ($CF_2$). IR spectrum: 608 sh, ms, 626 sh, w, 738 sh, s, 797 sh, s, 876 sh, s, 892 w, 913 sh, s, 1 017 w, 1 033 sh, vs, 1 100 sh, s, 1 156 sh, vs, 1 175 s, 1 183 s, 1 296 sh, vs, 1 375 w.

Trifluoroethyl Ethers *II* – *V*

The ethers *II*, *III*, *IV*, and *V* were obtained by chlorination of ether *XVI* up to a total consumption of 1.8 mol chlorine per 1 mol ether *XVI* (ref.[9]). The reaction mixture was rectified to give ether *V* with b.p. 110 °C, ρ 1.53 g $cm^{-3}$ (ref.[8] gives b.p. 104.4 °C/83.98 kPa, ρ 1.5269 g $cm^{-3}$), ether *IV* with b.p. 118 °C, ρ 1.58 g $cm^{-3}$ (ref.[10] gives b.p. 112.5 °C/83.44 kPa, ρ 1.5620 g $cm^{-3}$), ether *III* with b.p. 128 °C, ρ 1.63 g $cm^{-3}$ (ref.[9] gives b.p. 53 °C/6.67 kPa), and ether *II* with b.p. 137 °C, ρ 1.66 g $cm^{-3}$ (ref.[10] gives b.p. 131 °C/83.84 kPa, ρ 1.6631 g $cm^{-3}$).

*2-Chloro-1,1,2-trifluoroethyl trichloromethyl ether* (II). For $C_3HCl_4F_3O$ (251.9) calculated: 14.31% C, 0.40% H, 56.31% Cl, 22.63% F; found: 14.27% C, 0.39% H, 56.24% Cl, 22.38% F. MS, *m/z* (rel. int., %): 119 (55), 117 (100), 82 (17), 69 (13), 67 (36), 63 (75), 51 (9), 47 (9), 31 (12). $^1$H NMR spectrum: 6.14 dt, 1 H (CHFCl, $^2J$(H,F) = 48, $^3J$(H,F) = 5). $^{19}$F NMR spectrum: 46.30 m, 2 F ($CF_2$), 158.20 dt, 1 F (CHFCl, $^2J$(H,F) = 48, $^3J$(H,F) = 11). IR spectrum: 600 w, 707 sh, s 740 w, 797 vs, 808 vs, 864 sh, vs, 879 s, 912 w, 1 029 vs, 1 042 vs, 1 096 vs, 1 108 vs, 1 022 vs, 1 031 vs, 1 052 vs, 1 070 s, 1 244 sh, s, 1 258 s, 1 272 s, 1 284 sh, s, 1 361 sh, ms, 1 405 w, 2 985 w.

*2,2-Dichloro-1,1,2-trifluoroethyl dichloromethyl ether* (III). For $C_3HCl_4F_3O$ (251.9) calculated: 14.31% C, 0.40% H, 56.31% Cl, 22.63% F; found: 14.28% C, 0.40% H, 56.23% Cl, 22.37% F. MS, *m/z* (rel. int., %): 153 (75), 151 (100), 116 (18), 103 (28), 101 (43), 85 (58), 83 (76), 31 (22), 29 (27), 28 (19). $^1$H NMR spectrum: 7.43 s, 1 H ($CHCl_2$). $^{19}$F NMR spectrum: 76.01 t, 1 F ($CFCl_2$, $^3J$(F,F) = 10), 88.55 m, 2 F ($CF_2$). IR spectrum: 602 sh, ms, 713 sh, vs, 780 s, 853 w, 880 sh, s, 894 sh, s, 916 sh, vs, 1 002 ms, 1 023 sh, vs, 1 102 sh, vs, 1 148 vs, 1 180 vs, 1 227 sh, ms, 1 282 sh, vs, 1 340 w, 2 905 w.

*2-Chloro-1,1,2-trifluoroethyl dichloromethyl ether* (IV). For $C_3H_2Cl_3F_3O$ (217.4) calculated: 16.57% C, 0.93% H, 48.92% Cl, 26.22% F; found: 16.22% C, 0.93% H, 48.71% Cl, 26.14% F. MS, *m/z* (rel. int., %): 183 (24), 181 (28), 133 (27), 117 (97), 85 (66), 83 (100), 69 (10), 67 (61), 48 (23), 29 (41). $^1$H NMR spectrum: 6.16 dt, 1 H (CHFCl, $^2J$(H,F) = 48, $^3J$(H,F) = 5), 7.48 s, 1 H ($CHCl_2$). $^{19}$F NMR spectrum: 88.37 m, 2 F ($CF_2$), 155.17 dt, 1 F (CHFCl, $^2J$(H,F) = 48, $^3J$(F,F) = 11). IR spectrum: 678 sh, ms, 693 s, 699 s, 774 s, 793 s, 842 sh, ms, 875 sh, ms, 910 w, 1 010 s, 1 024 s, 1 094 vs, 1 118 vs, 1 153 vs, 1 167 vs, 1 224 sh, ms, 1 261 sh, vs, 1 257 sh, ms, 1 336 w, 1 369 sh, ms, 2 997 w.

*2-Chloro-1,1,2-trifluoroethyl chloromethyl ether* (V). For $C_3H_3Cl_2F_3O$ (183.0) calculated: 19.69% C, 1.65% H, 38.59% Cl, 31.15% F; found: 19.52% C, 1.60% H, 38.67% Cl, 31.02% F. MS, *m/z* (rel. int., %): 149 (24), 147 (70), 117 (70), 115 (27), 69 (33), 67 (100), 51 (63), 49 (61), 31 (34), 29 (28). $^1$H NMR spectrum: 5.66 s, 2 H ($CH_2Cl$), 6.12 dt, 1 H (CHFCl, $^2J$(H,F) = 48, $^3J$(H,F) = 5). $^{19}$F NMR spectrum: 69.0 m, 2 F ($CF_2$), 154.8 dt, 1 F (CHFCl, $^2J$(H,F) = 48, $^3J$(F,F) = 12). IR spectrum: 712 sh, ms, 731 ms, 804 sh, ms, 843 w, 862 sh, s, 992 sh, w, 1 023 ms, 1 040 ms, 1 095 vs, 1 116 vs, 1 147 vs, 1 162 vs, 1 252 sh, s, 1 278 sh, s, 1 291 ms, 1 342 w, 1 351 w, 1 372 sh, ms, 3 000 sh, w.

Photochemically Induced Reductions

The photochemical reactor of the effective volume given in Table I for the individual experiments was charged with the educt ethers *I* – *IV* or with their mixtures (the amounts are given in Table I). Cooling water was introduced into the cooled section of the reactor in such a way that the temperature of the outlet water did not exceed 10 – 12 °C immediately at the outlet from the reactor. The temperature of the reactor surface varied within the limits of 30 ± 3 °C. In the experiment No. 7 the reaction was carried out at 45 °C. The reactor was equipped with a sintered glass plate for introduction of gas, a reflux condenser with a freezing trap filled with a mixture of solid carbon dioxide and ethanol, and with a high pressure discharge

lamp Tesla RVK 125. A slow stream of nitrogen (50 ml/min) was introduced into the reactor in order to perfectly mix the reaction mixture in the whole volume of reactor. Samples (0.5 ml) were taken by means of a syringe and in the experiments Nos 7, 13, 14 they were analyzed immediately with special respect to the components with higher elution times (SE 301, 200 °C, 0.13 MPa $N_2$), whereafter they were shaken with water, and the small organic layer formed (ca 10 – 30 μl) was analyzed again by gas chromatography, this time with respect to relative proportions of halo ethers *I* – *V* in the reaction mixture (SE 301, 150 °C, 0.105 MPa $N_2$). The same procedure, i.e. shaking of the 0.5 ml sample with 2 ml water, was applied in all other experiments too. The results of chromatographic analyses are presented in graphs cited in Table I for the individual experiments. The ethers *II* – *V* formed in the reductions were identified by GLC (SE 301, 150 °C, 0.105 MPa $N_2$) by comparing with the standards of ethers *II* – *V* obtained by chlorination of ether *XVI* and by comparison of the IR and NMR spectra.

Ethers *VI* – *IX*

The distillation residues obtained from the photochemical reduction of ether *I* after distilling off the ethers *II* – *V* were steam distilled, dried with $MgSO_4$, and analyzed by GLC. It was found that they are mixtures of side products from which we could isolate ethers *VI* and *IX* by means of preparative GLC (SE 301, 197 °C, 35 ml $N_2$/min) and identify ethers *VII* and *VIII* by means of GLC-MS.

*1,2-Dichloro-1,2-bis(2-chloro-1,1,2-trifluoroethoxy)ethane* (VI). For $C_6H_4Cl_4F_6O_2$ (363.9) calculated: 19.81% C, 1.11% H, 31.33% F; found: 19.55% C, 1.45% H, 31.44% F. B.p. 80 – 82 °C/2.13 kPa. $^1$H NMR spectrum: 6.04 s, 1 H (CHCl), 6.08 dt, 1 H (CHClF, $^2J$(H,F) = 47.5, $^3J$(H,F) = 4.5). IR spectrum ($CCl_4$): 878 ms, 973 w, 1 029 ms, 1 097 sh, vs, 1 121 vs, 1 261 sh, s, 1 292 sh, s, 1 370 sh, ms, 1 453 w, 2 426 w, 2 924 w, 2 995 w.

*1-Chloro-1,2-bis(2-chloro-1,1,2-trifluoroethoxy)ethene* (VII). $C_6HCl_3F_6O$ (326.5). MS, *m/z* (rel. int., %): 326 (3.8, $M^+$), 258 (0.7), 209 (2), 193 (1.2), 181 (2), 174 (16), 133 (5), 117 (100).

*1,2-Dichloro-1,2-bis(2-chloro-1,1,2-trifluoroethoxy)ethene* (VIII). $C_6H_2Cl_4F_6O_2$ (361.9). MS, *m/z* (rel. int., %): 360 (1, $M^+$), 325 (0.2), 293 (0.4), 234 (0.2), 229 (3.4), 213 (4), 181 (1.5), 133 (8.5), 117 (100), 99 (10), 77 (12.6), 67 (4.2).

*3,6-Dichloro-5,5,6-trifluoro-2-methyl-4-oxa-2-hexanol* (IX). $C_6H_6Cl_2F_3O_2$ (241.0). B.p. 74 – 78 °C/80 Pa. MS, *m/z* (rel. int., %): 223 (0.6), 205 (1.3), 188 (2.7), 117 (10), 107 (2), 91 (11), 71 (16), 59 (100), 43 (58). $^1$H NMR spectrum: 1.40 s, 6 H ($CH_3$), 2.36 s, 1 H (OH), 6.28 dt, 1 H (CHFCl, $^2J$(H,F) = 46, $^3J$(H,F) = 5); 6.50 s (CHCl). IR spectrum: 542 w, 588 w, 560 w, 720 ms, 762 ms, 818 ms, 869 s, 1 020 ms, 1 095 vs, 1 110 vs, 1 150 vs, 1 254 s, 1 287 s, 1 321 w, 1 365 sh, ms, 1 464 w, 1 600 w, 1 683 w, 1 725 w, 1 763 w, 2 985 ms, 3 620 w.

Reduction of C–Cl Bonds Induced by γ Radiation with $^{60}$Co

Four glass ampoules of ca 6 ml volume were charged with 2.11 g (7.37 mmol) ether *I* and 4.478 g (74.5 mmol) 2-propanol each. The ampoules were sealed and exposed to γ-$^{60}$Co radiation, whereafter their content was analyzed by means of gas chromatography (SE 301, 150 °C, 0.11 MPa $N_2$). It was found that the starting ether *I* was completely transformed into the dichloromethyl ether *III* which did not undergo any further reduction. The resulting mixtures were not worked up.

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