

SELECTIVE PHOTOCHEMICAL REDUCTION OF CARBON-CHLORINE BOND IN FLUOROPROANOATES AND ITS QUANTUM YIELDS

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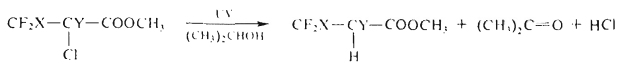
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Ultraviolet light initiated reduction of methyl 2,2,3-trichlorodifluoropropanoate (*I*), methyl 2,3-dichlorotrifluoropropanoate (*II*) and methyl 2-chlorotetrafluoropropanoate (*III*) in 2-propanol afforded methyl 2,3-dichloro-3,3-difluoropropanoate (*IV*), methyl 3-chloro-2,3,3-trifluoropropanoate (*V*) and methyl 2,3,3,3-tetrafluoropropanoate (*VI*) in the respective yields 81%, 86% and 75%. Maximum quantum yields, Φ_{\max} , of the reduction at 254 nm for the ester *IV*, *V* and *VI* are 225, 240 and 270, respectively, indicating thus a chain reduction mechanism.

Halogen-carbon bond reduction, initiated by UV radiation in proton-donating solvents, was utilized in a number of cases. This method was used in reduction of carbon-iodine¹, carbon-bromine^{2,3}, carbon-chlorine³⁻⁶ and also carbon-fluorine⁷ bonds. Fluorinated and halogenated alkanes¹⁻⁴, alcohols and 3-substituted trifluoropropanoates⁷ served as substrates. In the latter substrates, the C-F bond in position α , relative to the ester group was reduced. Since the reduction was slow, the amount of concurrently formed photochemical products was relatively large.

This communication concerns the photochemically initiated reduction of carbon-halogen bonds in fluorinated pentahalogenopropanoates *I-III*. All the esters contained chlorine in the position α to the ester group and the C-Cl bond was selectively reduced to give 2-hydriltetrahalogenopropanoates *IV-VI*. We used 2-propanol as reduction medium; however, the compounds *I-III* were reduced also in other solvents⁸ some of which had been used already previously. The reaction conditions and results are given in Table I. In addition to the fluorinated product, the reaction mixture contained acetone, hydrogen chloride and small amount of high-boiling compounds. At the end of the reaction there appeared small amounts of relatively volatile compounds in the mixture which were not identified. Complete conversion of the starting compounds was achieved after 80-120 min. The preparative yields of the products were obviously independent of concentration of the starting esters (in the range 1 : 5 to 1 : 20 in 2-propanol; Table I). Vigorous stirring of the reaction mixture appeared to be a significant preparative factor; without it the proportion of higher-boiling products increased. The mentioned reaction represents a preparation of fluorinated

2-hydryltetrahalogenopropanoates which is more facile than the hitherto known syntheses⁹⁻²⁰.



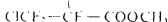
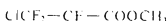
I-III

IV-VI

I, IV, X = Y = Cl

II, V, X = Cl, Y = F

III, VI, X = Y = F



VII

Quantum yields of photochemically initiated carbon-halogen bond reductions in aliphatic compounds in solvents have not been measured as yet. Several authors^{3,5,21} assume that this reaction has a chain mechanism, analogous *e.g.* to radical reduction of hexachloroethane with 2-propanol²². In reduction with 2-propanol, the reducing agent is assumed^{3,23,24} to be the ketyl radical, arising by loss of hydrogen atom from the alcohol. It is further assumed that the primarily formed intermediates are radicals arising by loss of halogen from the substrate^{3,21} which in the case of 2-halogeno esters were spectroscopically identified²¹. The finding of dimethyl 2,3-difluoro-2,3-bis-(chlorodifluoromethyl)butanedioate (VII) as the terminal product in the reduction of

TABLE I

Conditions and results of photochemical reduction of esters I-III

	Starting ester		2-Propanol ester	Irradiation time	Product	
	g	mol			mol : mol	g
I	9.7	0.043	15	65	IV 5.03	60.1
I	56.9	0.25	15	90	IV 31.5	65.2
I	68.2	0.30	15	100	IV 46.9	81.3
II	50	0.236	10	08	V 35.5	84.6
II	75	0.355	5	90	V 56.2	88.9
II	90	0.427	10	120	V 64.5	85.7
III	6.5	0.033	20	17	VI 2.63	49.8
III	13	0.067	10	30	VI 9.31	71.8
III	59	0.303	15	65	VI 36.4	75.5

the esters *I–III* confirms the presence of the assumed radical intermediates. The reaction mixture contained also pinacol which, however, could arise both by termination reaction²³ and by reaction²⁵ of 2-propanol with acetone.

Quantum yields of reduction of esters *I–III* were measured at 254 nm: at this wavelength 2-propanol absorbed negligibly in a 1 cm cell. Since the absorption maxima of the esters *I–III* were at 220–225 nm, we worked at relatively high concentrations (0.2 mol l^{-1}) to assure the total absorption up to about 40% conversion. The reaction was not sensitized by acetone (λ_{max} 273 nm, 2-propanol), on the contrary, its higher concentrations stopped the reaction. The reduction course in the monochromatic light was evaluated by gas-liquid chromatography and the quantum yields were calculated using the product curve (Fig. 1). There was an induction period at the beginning of the reaction; this was prolonged several times on addition of octylpyrocatechol which inhibits radical reactions. The course of reductions was followed in the range 4 000 to 7 000 s. The quantum yields were calculated for the interval of 2 000 s in the most steep part of the product curves. For products *IV*, *V* and *VI* the quantum yields ϕ_{max} amounted to 225, 240 and 270, respectively (means of two measurements). This result, together with the identification of the terminal product *VII*, confirms the chain mechanism of the studied reaction.

EXPERIMENTAL

Temperature data are uncorrected. Gas-liquid chromatography was performed on a Chrom 41 instrument (Laboratorní přístroje, Prague; flame-ionization detector, integrator, stainless steel columns of internal diameter 0.3 cm, support Chromaton N-AW-DMCS (Lachema, Brno); carrier gas nitrogen). IR spectra were taken on a Perkin-Elmer 325 spectrophotometer (Bodensee-werk), UV spectra on a Specord UV-VIS (Zeiss, Jena) instrument. Measurements of NMR spectra

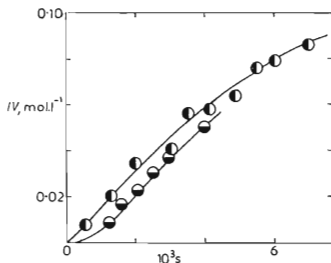


FIG. 1
Course of reduction of the ester *I* in quantum yield measurement (starting concentration of *I* 0.2 mol l^{-1} in both cases)

were performed on Varian XL-100-15 (Palo Alto) and Tesla BS 567 (Brno) instruments; chemical shifts given in ppm, coupling constants J in Hz, solvent deuteriochloroform; for ^{19}F NMR internal standard CCl_3F . Mass spectra were taken on a one-focus LKB 9000 spectrometer (Stockholm); chromatographic inlet SE 30 on Chromaton N-AW, glass column 250×0.23 cm, carrier gas helium.

Actinometric apparatus: A UV lamp RWK 250 W (Tesla) with parabolic reflector served as the light source. The light passed through a four-faced housing, containing a quartz lens, 5 cm thick layer of nickel sulfate solution²⁶, a UG 5 region glass filter (Schott, Jena), 1 cm layer of iodine-potassium iodide solution²⁶, adjustable slit, mechanical shutter and quartz lens. The parts of this set were separated by slits; the monochromatic light was concentrated into a four-faced cell of 1 cm thickness (Pye, Cambridge), equipped with a magnetic stirrer. The cell was closed by a modified teflon stopper containing a septum for sample withdrawal. Intensity of the monochromatic light (254 nm) in the cell was $I_0 = 2.3-2.8 \times 10^{-10}$ mol quanta s^{-1} (Einstein s^{-1}).

Chemicals: Tripotassium-ferric tris(oxalate) ("ferrioxalate") was prepared²⁷ at Technische Hochschule Leuna-Merseburg. 2-Propanol was dried over calcium oxide (about 10% wt) for 3 days, fractionated from phosphorus pentoxide and stored over molecular sieve (Potasit 3). Methyl 2,2,3-trichloro-3,3-difluoropropanoate²⁸ (*I*), methyl 2,3-dichloro-2,3,3-trifluoropropanoate^{28,29} (*II*) and methyl 2-chloro-2,3,3,3-tetrafluoropropanoate^{30,31} (*III*) were prepared according to previously described procedures. Ester *II* contained about 7% of two other isomers.

Preparative Reduction of *I-III*

A mixture of the propanoate (*I*, *II* or *III*) and 2-propanol was irradiated with a UV-lamp (RVK 125 W, Tesla) in an immersion-well quartz reactor at 18–20°C. The mixture was stirred by passing nitrogen into the mixture. The reaction course was followed by gas-liquid chromatography. After all the starting propanoate had been reacted, the mixture was poured on ice. The organic layer was separated, washed successively with ice-cold water, 20% calcium chloride solution and again with water and dried over magnesium sulfate. Fractionation of the crude product afforded the ester *IV*, *V* or *VI*; the reaction conditions and yields are given in Table I.

Gas-liquid chromatography: esters *I* and *IV*: 15% poly(propanediol sebacate), column 250 cm, 125°C; esters *II* and *V*: 15% poly(butanediol succinate), column 370 cm, 156°C; esters *III* and *VI*: 15% Carbowax 6 000, column 370 cm, 83°C.

IR spectra (carbon disulfide, tetrachloromethane, cm^{-1}): compound *IV*: 818 m, 983 s, 1 016 m, 1 035 m, 1 110 s, 1 165 m, 1 195 m, 1 212 m, 1 268 s, 1 336 m, 1 437 m; 1 758 s and 1 775 s $\nu(\text{C}=\text{O})$, 2 855 w, 2 975 w, 3 012 w $\nu(\text{C}-\text{H})$; compound *V*: 985 s, 1 020 m, 1 055 s, 1 135 s, 1 175 m, 1 210 m, 1 230 m, 1 290 m, 1 320 m, 1 355 m, 1 442 m, 1 769 s and 1 787 s $\nu(\text{C}=\text{O})$, 2 860 w, 2 973 w, 3 015 w $\nu(\text{C}-\text{H})$; compound *VI*: 985 m, 1 015 m, 1 104 m, 1 148 s, 1 200 s, 1 226 s, 1 245 m, 1 278 s, 1 298 s, 1 322 m, 1 345 m, 1 365 m, 1 445 m, 1 767 s and 1 787 s $\nu(\text{C}=\text{O})$, 2 966 w, 3 016 w $\nu(\text{C}-\text{H})$.

NMR spectra (s singlet, d doublet, t triplet, q quartet, m multiplet), compound *IV*: ^1H spectrum: s (3) 3.89 (OCH_3); t (1) 4.78 (CHCl), $^3J_{\text{HF}}$ 9 and 7; ^{19}F spectrum: dd (1) -61.3 and dd (1) -57.8, (CClF_2); $^2J_{\text{FF}}$ 164; compound *V*: ^1H spectrum: s (3) 3.89 (OCH_3), dt (1) 5.11 (CHF); $^2J_{\text{HF}}$ 46, $^3J_{\text{HF}}$ 6.5 and 7.5; ^{19}F spectrum: dt (1) -196.3 (CHF), $^3J_{\text{FF}}$ 17; ddd (1) -65, ddd (1) -62.4 (CClF_2), $^2J_{\text{FF}}$ 174; compound *VI*: ^1H spectrum: s (3) 3.81 (OCH_3), dq (1) 5.03 (CHF), $^2J_{\text{HF}}$ 46, $^3J_{\text{HF}}$ 6.8; ^{19}F spectrum: dq (1) -205.7 (CHF), dd (3) -76.9 (CF_3), $^3J_{\text{FF}}$ 12.

UV spectra ($\lambda_{\text{max}}/\epsilon$): in methanol: *II* 221/1 450, *IV* 214/880, *V* 216/960, *VI* 215/840; in 2-propanol: *I* 224/1 065, *II* 223/1 040, *III* 224/950.

For compound *IV*, $C_4H_4Cl_2F_2O_2$ (193.0) calculated: 24.89% C, 2.09% H, 36.74% Cl, 19.69% F; found: 23.89% C, 2.17% H, 36.27% Cl, 19.77% F. For compound *V*, $C_4H_4ClF_3O_2$ (176.5) calculated: 27.22% C, 2.28% H, 20.08% Cl, 32.29% F; found: 27.74% C, 2.43% H, 20.38% Cl, 32.04% F. For compound *VI*, $C_4H_4F_4O_2$ (159.0) calculated: 30.15% C, 2.53% H, 47.48% F; found: 30.65% C, 2.35% H, 47.29% F.

Higher-boiling material from distillation of *V* afforded a fraction boiling at 140–155°C/13 Pa, consisting of two principal compounds of identical mass spectra. These products are probably the diastereoisomeric compounds *VII*. Mass spectrum (principal ions, *m/e*, relative intensity, %): $(M - OCH_3)^{+}$ 319/1.8, $(M - Cl)^{+}$ 315/2.1, $(M - Cl, CO_2)^{+}$ 271/7.7, $(M - CClF_2, CO_2)^{+}$ 221/21, $(C_4ClF_4O)^{+}$ 175/2.4, $(C_5H_3F_4O_2)^{+}$ 171/4, $(C_3H_3F_2O_2)^{+}$ 109/5.1, $(C_3ClF_4)^{+}$ 147/8.5, $(C_2ClF_2)^{+}$ 97/2.3, $(C_3F_3)^{+}$ 93/7.7, $(CClF_2)^{+}$ 85/8.5, $(C_2F_3)^{+}$ 81/9.5, $(COOCH_3)^{+}$ 59/100.

Measurement of Light Intensity and Quantum Yields

Intensity of the monochromatic (254 nm) light was measured using the ferrioxalate actinometer^{27,32,33}. Quantum yields were measured as follows: Dry nitrogen was introduced into a solution of the ester (*I–III*) in 2-propanol (2.5 ml; 0.2 mol l⁻¹) for 15 min at -40°C and for 5 min at room temperature. Before entering the reaction cell, the nitrogen was bubbled through a solution of the same composition. During the irradiation samples were withdrawn by means of a microsyringe; 2 μl of nitrogen were injected and 1.5 μl of sample was withdrawn. Concentration of the products *IV–VI* in the reaction mixture was determined using a calibration graph (the chromatographic response of the starting compounds was stronger than that of the products).

The spectral measurements were performed in the Laboratory of NMR spectrometry (Dr P. Trška, Head), Laboratory of IR spectroscopy (Dr A. Muck, Head) and Laboratory of mass spectrometry (Dr V. Kubelka, Head); the elemental analyses were carried out in the Department of organic analysis (Dr L. Helešic, Head) of this Institute.

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