

CHEMISTRY OF ORGANIC FLUORINE COMPOUNDS. XI.*
PHOTOCHEMICAL ADDITION OF ETHANOL
AND 1-PROPANOL TO TRIFLUOROCHLOROETHYLENE

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The addition of ethanol to trifluorochloroethylene, initiated by ultraviolet radiation, gave the same products as the reaction initiated by organic initiators and γ -radiation ^{60}C . During the photochemical addition of 1-propanol trifluorochloroethylation on α - and β -CH bonds takes place giving rise to two 1 : 1 adducts — 1,2,2-trifluoro-1-chloro-3-pentanol (*IX*) and 2-methyl-3,3,4-trifluoro-4-chloro-1-butanol (*XII*). Among other products 4,4,5,6,6,7-hexafluoro-5,7-dichloro-3-heptanol (*X*, 1 : 2 telomer) and 4,4,5,6,6,7-hexafluoro-5,7-dichloro-3-heptanone (*XI*) were also isolated. IR and PMR spectra of these compounds are also given.

We described the radical addition of ethanol to trifluorochloroethylene initiated by organic initiators and γ -radiation ^{60}Co earlier¹. This time we used UV radiation^{2,3} for the initiation of the addition. Making use of gas chromatography, *i.e.* comparing the elution times with standards¹, we found that the same products were formed as in cases when the initiation was carried out by organic initiators of γ -radiation ^{60}Co . The following addition and telomeric products were formed: 3,3,4-trifluoro-4-chloro-2-butanol (*I*, 1 : 1 adduct), 3,3,4,5,5,6-hexafluoro-4,6-dichloro-2-hexanol (*II*, 1 : 2 telomer), and 3,3,4,5,5,6,7,7,8-nonafluoro-4,6,8-trichloro-2-octanol (*III*, 1 : 3 telomer). The products which were formed on rearrangement of the 1 : 2 telomer radical are: 3,3,4,5,5,6-hexafluoro-4,6-dichloro-2-hexanone (*IV*) and 3-methyl-1,2,2,4,4,5,6,6,7-nonafluoro-1,5,7-trichloro-3-heptanol (*V*). According to gas chromatography the 1 : 2 telomer *II* was accompanied by a substance with a shorter elution time which was identified as 3,3,4,5,5,6-hexafluoro-6-chloro-2-hexanol (*VI*) on comparison with a standard substance obtained on photochemical reduction of alcohol *II* in 2-propanol solution⁴. The reaction conditions and the results of the addition of ethanol are represented in Table I.

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TABLE I
Addition of Alcohols R-OH to Trifluorochloroethylene

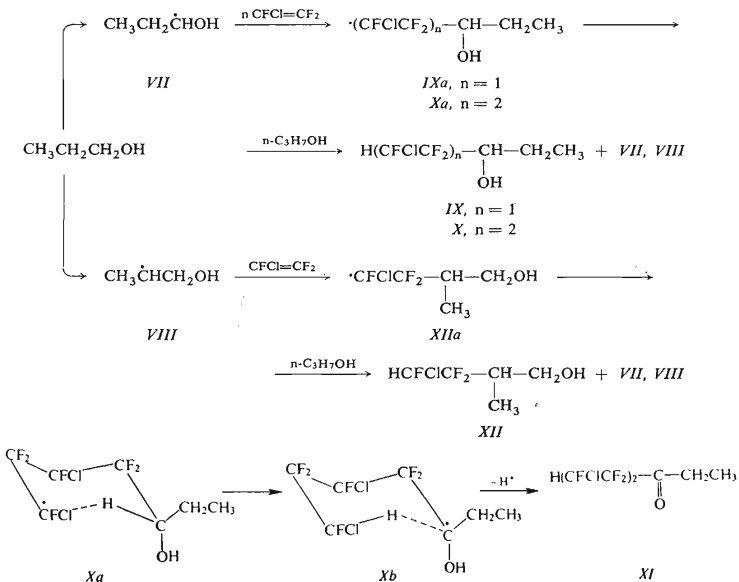
R (g) Procedure	CFCI=CF ₂ g, (h)	°C (time, h)		Reaction products, g	Distil- lation residue, g
C ₂ H ₅ B	59 (0-35)	15 (36)	11-8 I ^a	0-3 III ^a 0-4 IV ^a	0-2 VI ^a 6
n-C ₃ H ₇ A	112 (0-77)	97 (30)	20-9 IX ^b	0-2 X ^a 0-4 XI ^a	2-5 XII ^a 3-3
n-C ₃ H ₇ B	127 (0-61)	30	11-3 IX ^b	2-3 X ^a 0-8 XI ^a	3-4 XII ^b 16-9
n-C ₃ H ₇ C	240-4	50 (52)	15-4 IX ^b	13-2 X ^b 8-4 XI ^b	7-3 XII ^b 110

^a Calculated from the chromatograms, ^b sum of the weight of products obtained by distillation and the amount from the chromatograms of intermediate fractions, ^c sum of the content in all three ampoules.

The formation of single products can be explained by an analogous mechanism as in the case of the initiation by γ -radiation $^{60}\text{Co}^1$. We assume that the reaction is started by the 1-hydroxyethyl radical ($\text{CH}_3\dot{\text{C}}\text{HOH}$) the addition of which to trifluorochloroethylene and subsequent addition and transfer reactions of the formed adduct-radicals lead to the formation of products I–V. Alcohol VI is probably formed as a secondary product of the reaction by reductive elimination of the chlorine atom in the 1 : 2 telomer II with ethanol under conditions⁴ of radical reactions.

After the radical addition of 1-propanol to trifluorochloroethylene, initiated by UV radiation, two 1 : 1 adducts were isolated, i.e. 1,2,2-trifluoro-1-chloro-3-pentanol (IX) and 2-methyl-3,3,4-trifluoro-4-chloro-1-butanol (XII). Among other products the 1 : 2 telomer 4,4,5,6,6,7-hexafluoro-5,7-dichloro-3-heptanol (X) and 4,4,5,6,6,7-hexafluoro-5,7-dichloro-3-heptanone (XI) were also identified. The reaction conditions and the results of the addition of 1-propanol are given in Table I.

The formation of the products can be explained by the mechanism proposed by Urry and coworkers⁵ for the radical addition of alcohols to olefins (Scheme 1).



SCHEME 1

TABLE II
Elemental Analyses and IR Spectra of Products of Addition of 1-Propanol to Trifluorochloroethylene

Compound (b.p., °C/Torr)	Formula (mol.w.)	Calculated/Found			IR Spectra, cm ⁻¹
		% C	% H	% Cl	
IX (50/9)	C ₃ H ₈ ClF ₃ O (176.6)	34.01	4.57	20.08	832 w, 858 s, 897 w, 912 w, 989 s, 1024 ms, 1039 s, 1059 sh, s 1075 vs, 1089 vs, 1125 s, 1191 s, 1235 s, 1280 w, 1312 w, 1354 w, 1383 ms, 1450 sh, ms, 1466 ms—2750 ms, 2889 s, 2946 vs, 2980 vs, 3410 vs, 3602 s
		34.22	4.53	20.26	
X	C ₇ H ₈ Cl ₂ F ₆ O (293.0)	28.69	2.75	24.20	833 w, 860 ms, 900 w, 943 s, 994 ms, 1050 ms, 1075 sh, ms, 1100 vs, 1120 vs, 1147 vs, 1168 sh, ms, 1195 sh, ms, 1232 s, 1246 sh, ms, 1313 ms, 1354 w, 1396 w, 1455 w, 1469 w—2888 s, 2947 vs, 2982 vs, 3420 vs, 3602 s, 3630 sh, s
		28.64	2.90	24.24	
XI	C ₇ H ₆ Cl ₂ F ₆ O (291.0)	28.89	2.08	24.36	833 sh, w, 848 ms, 858 ms, 886 ms, 935 sh, ms, 945 ms, 972 ms, 1020 ms, 1098 vs, 1107 sh, vs, 1137 s, 1160 vs, 1200 s, 1233 s, 1357 ms, 1391 vs, 1413 ms, 1468 ms, 1767 s,—2891 s, 2920 sh, s, 2950 s, 2992 s, 3495 ms, 3600 ms
		27.45	2.08	24.09	
XII (71/10)	C ₃ H ₈ ClF ₃ O (176.6)	34.01	4.57	20.08	848 s, 884 w, 903 w, 935 w, 990 sh, ms, 1017 s, 1034 s, 1077 vs, 1099 s, 1150 ms, 1190 ms, 1222 s, 1286 w, 1300 w, 1353 w, 1382 w, 1470 ms—2898 vs, 2956 vs, 2986 vs, 3400 vs, 3631 s
		34.28	4.75	20.29	

We suppose that on UV irradiation of a trifluorochloroethylene solution in 1-propanol homolytic cleavage of the α -C—H bond in the 1-propanol molecule takes place under formation of 1-hydroxy-1-propyl radical *VII* which on addition to the difluoromethylene group of olefin gives the 1 : 1 adduct-radical *IXa*. The radical *IXa* forms the 1 : 1 adduct *IX* by the chain transfer to 1-propanol, or, by addition to another olefin molecule it gives the 1 : 2 adduct-radical *Xa* which is then transformed to the 1 : 2 telomer *X* by the chain-transfer to the solvent. The radical *Xa* can also form a new 1 : 2 adduct-radical *Xb* by an intramolecular 1,5-transfer of the α -hydrogen atom^{1,3}. The adduct radical *Xb* can then give ketone *XI* on departure of the hydrogen atom. The formation of the primary alcohol *XII* can be explained by the homolytic cleavage of the β -C—H bond in the molecule of 1-propanol and by the formation of 1-hydroxy-2-propyl radical *VIII* which on addition to trifluorochloroethylene gives rise to the 1 : 1 adduct-radical *XIIa*. The latter transfers its chain to 1-propanol giving rise to alcohol *XII* and a new solvent-radical *VII* or *VIII*. The homolytic cleavage of the β -C—H bond was also demonstrated experimentally in the case of 2-methyl-2-butanol⁶ and during the addition of alcohols to β -pinene initiated by di-tert-butyl peroxide⁷.

TABLE III
PMR Spectra of Fluorochloroalknols *IX*, *X*, *XII*, and Ketone *XI*

Information	Compound ^a			
	<i>IX</i>	<i>X</i>	<i>XI</i>	<i>XII</i>
HCFCI—	3.68 (2 dd)	3.44 (dm)	3.43 (dm)	3.70 (dt)
	3.71 (2 dd)			3.65 (2dd)
H—C	6.15 (m)	5.90 (m)	—	7.57 (m)
H—C—H	8.35 (m)	8.30 (m)	7.19 (q)	6.34 (d)
				6.30 (d)
H ₃ C—	8.94 (t)	8.94 (t)	8.82 (t)	8.88 (d)
H—O—	7.30 (s)	7.28 (s)	—	7.10 (s)
² J _{HF}	47.0	47.5	46.8	48.5
	48.5			47.0
³ J _{HF}	5 a 10	—	—	7.5
	9 a 6.5			11 a 4
³ J _{CH₂CH}	—	—	—	6.5
				6.5
³ J _{CH₃CH}	—	—	—	7.0
³ J _{CH₃CH₂}	7.2	7.5	7.3	—

^a The values of signals are given in τ -units: dd (doublet of doublets), m (multiplet), dt (doublet of triplets), d (doublet), t (triplet), s (singlet), q (quartet); the values of coupling constants are given in Hz.

The structure of products *IX–XII* was proved by elemental analysis and by IR spectra (Table II). The PMR spectra also corroborated the proposed structures (Table III). In addition to this the identity of alcohol *XII* with the alcohol obtained on hydroboration reaction of 2-methyl-3,3,4-trifluoro-4-chloro-1-butene⁸ was also demonstrated. The PMR spectra of compounds *IX–XII* show that they are a mixture of diastereoisomers, which is in agreement with the fact that they contain two or three centers of chirality. The signals of protons of the —CHClF group be identified for single diastereoisomeric racemates only in the case of alcohols *IX* and *XII*; in other cases only the average values of chemical shifts are given.

EXPERIMENTAL

Temperature data are not corrected. The IR spectra were measured on a Zeiss, Jena UR-10 apparatus in tetrachloromethane ($800\text{--}2000\text{ cm}^{-1}$) and as liquid samples ($2600\text{--}3700\text{ cm}^{-1}$). The PMR spectra were measured on Tesla BS 477 (60 MHz) and Tesla BS 478 (80 MHz) spectrographs in tetrachloromethane solution with hexamethyldisiloxane as internal standard. Gas chromatographic analyses were carried out on a Chrom II apparatus (FID) and preparative gas chromatography was performed on an apparatus of non-commercial origin. In both cases poly(propylene sebacate) on Celite 455 was the stationary phase and nitrogen served as the carrier gas.

Chemicals Used

Trifluorochloroethylene was of commercial origin, producer Spolek pro chemickou a hutní výrobu, Ústí nad Labem. Ethanol and 1-propanol were pure grade.

Photochemical Additions

A) *Under flowing trifluorochloroethylene at boiling point of alcohol*: A quartz ampoule of approx. 180 ml volume, provided with a reflux condenser and a sintered glass filtration tube for the introduction of olefin was filled with 1-propanol and trifluorochloroethylene was introduced into it from a pressure vessel *via* a flow-meter. The ampoule was irradiated by an ultraviolet lamp (Tesla 400 W) from a 5 cm distance.

B) *Under flowing trifluorochloroethylene at 20–30°C*: Alcohol was introduced into a glass reactor provided with a reflux condenser, a sintered-glass filtration tube for the introduction of olefin, and a water-cooled mercury lamp (Tesla 80 W, with a quartz filter), and trifluorochloroethylene was introduced into it *via* a flow-meter. The temperature of the reaction mixture was kept at 20–30°C by the water-cooling system of the mercury lamp.

C) *Under higher pressure in a closed system*: A quartz ampoule of 250 ml volume was filled with 96.9 g of 1-propanol and then rinsed with nitrogen and evacuated with a water pump. Trifluorochloroethylene (87.8 g) from a gas-container (dried by anhydrous magnesium perchlorate) was introduced and condensed into the ampoule which was then sealed. In a similar manner two additional quartz ampoules were filled with 96.9 g and 98.2 g of 1-propanol and 83.5 and 69.1 g of trifluorochloroethylene, respectively. The ampoules were irradiated with a Tesla 400 W mercury lamp from a distance of 7 cm. They were then cooled in a mixture of dry ice and ethanol and opened. Warming at an ambient temperature caused the evaporation of the unreacted olefin. The content of all three ampoules was combined and worked up.

Working up of the Reaction Mixtures

The reaction mixtures from single experiments were rectified. After the distillation of the unreacted alcohol the residue was fractionated and single fractions were submitted to gas-chromatographic analysis. The total amounts of products listed in Table I represent the sum of the products obtained by distillation and the products present in intermediate fractions, calculated from chromatograms of these fractions. The amounts of the samples, the reaction conditions, and the results of the additions are presented in Table I.

Addition of ethanol to trifluorochloroethylene (procedure B): Distillation of the reaction mixture after addition gave 12.6 g of a fraction boiling at 95–130°C, 3.9 of a fraction of b.p. 42–80°C/9 Torr, 3.6 of a fraction b.p. 80–120°C/9 Torr, and 6 g of the distillation residue. The reaction products were identified gas-chromatographically on comparison of their elution times with those of standards^{1,3}.

Addition of 1-propanol to trifluorochloroethylene: From the addition initiated according to A 22.5 g of a fraction was obtained, b.p. 50–59°C/10 Torr, which according to gas-chromatography contained alcohol IX as the main product. Fractions of a similar composition (from procedure B) were combined with it and submitted to rectification which gave pure alcohol IX, b.p. 50°C/9 Torr, and a residue distilling between 59° and 70°C/10 Torr. This residue was a mixture of pentanol IX and butanol XII. Alcohol XII was isolated in pure state by preparative gas chromatography. From experiment C 14.6 g of a fraction, b.p. 70–90°C/10 Torr, were obtained which contained approx. 50% of alcohol X. Repeated rectification produced an enriched (80%) alcohol X, b.p. 96–99°C/21 Torr. Alcohol X was obtained by preparative gas chromatography in pure state. From the experiment C 24.4 g of the fraction boiling at 59–70°C/12 Torr were obtained, which was composed according to gas chromatographic analysis predominantly of a mixture of alcohols IX and XII and of approximately 20% of ketone XI which was obtained in pure state by preparative gas chromatography.

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