

CHEMISTRY OF ORGANIC FLUORINE COMPOUNDS. XIII.\*  
 RADICALIC ADDITION OF 2-PROPANOL AND 2-BUTANOL  
 TO TRIFLUOROCHLOROETHYLENE

F. LIŠKA, M. NĚMEC and V. DĚDEK

*Department of Organic Chemistry,  
 Institute of Chemical Technology, Prague 6*

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It was shown that on photochemical addition of 2-propanol to trifluorochloroethylene the same products are formed as when initiation was carried out with organic initiators or  $^{60}\text{Co}$ - $\gamma$ -radiation. From the addition of 2-butanol initiated by ultraviolet and  $^{60}\text{Co}$   $\gamma$ -radiation telomeric alcohols 3-methyl-4,4,5,6,6,7-hexafluoro-5,7-dichloro-3-heptanol (*XI*) and 3-methyl-4,4,5,6,6,7,8,8,9-nonafluoro-5,7,9-trichloro-3-nonanol (*XII*) were isolated in addition to 3-methyl-1,2,2-trifluoro-1-chloro-3-pentanol (*IX*). As reduction products 3-methyl-4,4,5,6,6,7-hexafluoro-7-chloro-3-heptanol (*XIII*) and 3-methyl-4,4,5,6,6,7,8,8,9-nonafluoro-9-chloro-3-nonanol (*XIV*) were identified. Alcohols *XIII* and *XIV* were also prepared by photochemical reduction of alcohols *XI* and *XII* with 2-propanol. 1 : 1 Adducts from the addition of 2-propanol (*I*) and 2-butanol (*IX*) are accompanied by isomeric 2-methyl-3,4,4-trifluoro-3-chloro-2-butanol (*II*) and 3-methyl-1,1,2-trifluoro-2-chloro-3-pentanol (*X*) the structure of which was determined on the basis of mass spectra.

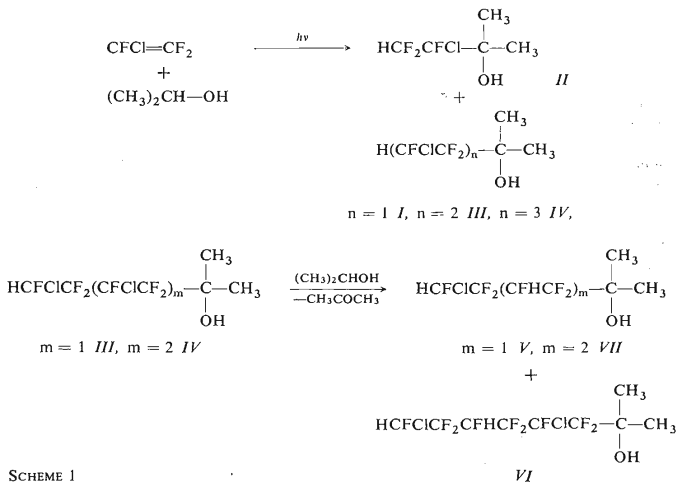
In the paper<sup>1</sup> we described the addition of 2-propanol to trifluorochloroethylene, initiated by organic initiators and  $^{60}\text{Co}$   $\gamma$ -radiation. In the present investigation we used ultraviolet radiation<sup>2-5</sup> for the same reaction and identified the reaction products by comparison of their elution times with standards. The telomeric and addition products formed are 2-methyl-3,3,4-trifluoro-4-chloro-2-butanol (*I*), 2-methyl-3,3,4,5,5,6-hexafluoro-4,6-dichloro-2-hexanol (*III*) and 2-methyl-3,3,4,5,5,6,7,7,8-nonafluoro-4,6,8-trichloro-2-octanol (*IV*), and alcohols formed on reduction of chlorine atoms in the primarily formed 1 : 2 and 1 : 3 telomers *III* and *IV*, such as 2-methyl-3,3,4,5,5,6-hexafluoro-6-chloro-2-hexanol (*V*), 2-methyl-3,3,4,5,5,6,7,7,8-nonafluoro-4,8-dichloro-2-octanol (*VI*), and 2-methyl-3,3,4,5,5,6,7,7,8-nonafluoro-8-chloro-2-octanol (*VII*).

The formation of single products may be explained in an analogous manner as when the initiation was carried out with organic initiators and  $^{60}\text{Co}$   $\gamma$ -radiation<sup>1</sup>. Here only the overall reaction scheme is presented.

We tried to propose a structure for the substance with a shorter elution time, which accompanies alcohol *I* in a 5% concentration. The comparison of its mass spectrum with that of alcohol *I*

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suggested that it is a structural isomer of alcohol *I*, i.e. 2-methyl-3,4,4-trifluoro-3-chloro-2-butanol (*II*) the formation of which may be explained by the addition of 2-hydroxy-2-propyl radical to  $\text{CFCl}=\text{CF}_2$  group<sup>3</sup> in the molecule of trifluorochloroethylene, and subsequent transfer of the chain to 2-propanol. In the mass spectra of both alcohols the molecular ion  $\text{M}^+$  is not present but ions  $m/e$  161 ( $\text{M}^+ - 15$ ) and 163 appear in a 3 : 1 ratio which corresponds to the presence of one chlorine atom in the molecule<sup>6</sup>. The mass spectra of substance *I* and *II* differ only in relative intensity of single ionic species, but not in their  $m/e$  values. The main ionic species of alcohol *I* is  $m/e$  59 (100%) which is accompanied by intense ions  $m/e$  (% of relative intensity) 43 (74%), 31 (40%), 41 (18%), 65 (10%). In contrast to this the main ionic species of alcohol *II* is  $m/e$  43 (100%), accompanied by ions of  $m/e$  59 (80%), 31 (30%), 41 (14%), 161 (12%), and 65 (9.3%).



SCHEME 1

After photochemical addition of 2-butanol to trifluorochloroethylene we isolated 3-methyl-1,2,2-trifluoro-1-chloro-3-pentanol (1 : 1 adduct, *IX*), 3-methyl-4,4,5,6,6,7-hexafluoro-5,7-dichloro-3-heptanol (1 : 2 telomer, *XI*), and 3-methyl-4,4,5,6,6,7,8,8,9-nonafluoro-5,7,9-trichloro-3-nonanol (1 : 3 telomer, *XII*) as the main products. In this case too the 1 : 1 adduct *IX* was accompanied by 5% of a substance with a shorter elution time which was identified as 3-methyl-1,1,2-trifluoro-2-chloro-3-pentanol (*X*) on the basis of the comparison of its mass spectrum with that of alcohol *IX*.

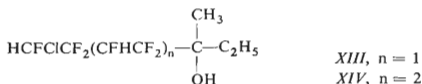
The mass spectra of both alcohols are very similar. In neither of them is the molecular ion present, but they contain the ions of  $m/e$  175 ( $\text{M}^+ - 15$ ) and 177 and 161 ( $\text{M}^+ - 29$ ) and 163. From the ratios of ionic species in single pairs it may be concluded that they contain a chlorine atom<sup>6</sup>. The main ionic species in both spectra is ion  $m/e$  43 (100%). Of other ions the following are more abundant

(for alcohol *IX*): *m/e* (% of relative intensity) 73 (83%), 55 (41%), 161 (25%), 29 (23%), 57 (15%), 45 (12%), 31 (10%), 163 (8.4%). For alcohol *X*: 73 (71%), 55 (43%), 161 (37%), 29 (28%), 45 (14%), 51 (14%), 57 (14%), 31 (13%), 77 (12%), 163 (12%), 41 (11%). The transformation of ions *m/e* 161<sup>+</sup> → 141<sup>+</sup> and *m/e* 73<sup>+</sup> → 55<sup>+</sup> is corroborated by metastable ions.

For the explanation of the formation of single products a radical reaction course is assumed, similar to that during the addition of 2-propanol<sup>1</sup>.

The reaction is probably initiated by 2-hydroxy-2-butyl-radical (*VIII*) which is formed by the interaction of the ultraviolet or <sup>60</sup>Co  $\gamma$ -radiation with a solution of trifluorochloroethylene in 2-butanol. Radical *VIII* is then added to both sides of the double bond in trifluorochloroethylene under formation of two 1 : 1 adduct radicals *IXa* or *Xa*. They form the 1 : 1 adducts *IX* and *X* by a transfer of the chain on the solvent molecules. On the basis of their ratio (approx. 95 : 5) it is evident that the addition practically takes place only to =CF<sub>2</sub> group in the olefin molecule. The 1 : 1 adduct radical *IXa* also undergoes a telomerisation reaction with other olefin molecules and forms thus 1 : 2 (*XIa*), 1 : 3 (*XIIa*) and up to 1 : *n* adduct radicals of which each creates by a chain transfer 1 : 2 (*XI*), 1 : 3 (*XII*), or 1 : *n* telomers, and the new radical *VIII*. We do not consider an analogous transformation of the adduct radical *Xa* because we were unable to demonstrate alcohols of a corresponding structure in the reaction mixture.

We determined gas chromatographically that the 1 : 2 telomer *XI* is accompanied by one, and the 1 : 3 telomer *XII* by three substances of a shorter elution time. These substances are probably formed as secondary reaction products by reduction of the C—Cl bonds in —CFCl-groups<sup>1,7</sup> of the fluorochloroalkyl chain in 1 : 2 (*XI*) and 1 : 3 (*XII*) telomers with 2-butanol under radicalic conditions. Two of these substances were prepared by irradiation of the solutions of alcohols *XI* and *XII* in 2-propanol by ultraviolet radiation<sup>7</sup>, and they were identified as 3-methyl-4,4,5,6,6,7-hexafluoro-7-chloro-3-heptanol (*XIII*) and 3-methyl-4,4,5,6,6,7,8,8,9-nonafluoro-9-chloro-3-nonanol (*XIV*). The alcohols *XIII* and *XIV* were chromatographically identical with the substances accompanying telomers *XI* and *XII* in the reaction mixture.



The alcohols which would be formed by reduction of a single chlorine atom in the 1 : 3 telomer *XII* only, were not isolated from the reaction mixture. They are probably the two remaining substances (Table I, *XIVa*) which accompany the alcohol *XII* in the reaction mixture in gas chromatographic analysis and which on further irradiation are transformed to alcohol *XIV*. On the basis of the structure of the isolated reaction products and on the basis of earlier results<sup>7</sup> it may be stated that the reduction of the chlorine atom in the terminal —CFClH group does not take place.

TABLE I  
Addition of Alcohols  $\text{CH}_3\text{CH}(\text{OH})\text{R}$  to Trifluorochloroethylene

Alcohol, g (olefin, g; 1/h)	Initiation (method)	Temperature °C (time, h)	Products g			Residue
			<i>I</i> + <i>II</i> <sup>a</sup> ( <i>III</i> )	<i>IV</i> ( <i>V</i> )	<i>VI</i> ( <i>VII</i> )	
<b>R = CH<sub>3</sub></b>						
78.5 (81.5; 1.9)	UV (A)	80 (9)	89.15 (0.18)	0.03 (0.13)	—	1.13
79.0 (97.0; 1.7)	UV (B)	20 (12)	66.42 (9.39)	1.44 (5.68)	1.18 (2.13)	7.50
58.2 (35.5)	$\gamma\text{-}^{60}\text{Co}$ —	20 (3.82)	20.70 (8.16)	6.70 (1.0)	2.16 —	1.60
<b>R = C<sub>2</sub>H<sub>5</sub></b>						
			<i>IX</i> + <i>X</i> <sup>b</sup> ( <i>XI</i> )	<i>XII</i> ( <i>XIII</i> )	<i>XIVa</i> ( <i>XIV</i> )	Residue
113.0 (28.6; 1.0)	UV (B)	20 (6)	22.08 (2.17)	— (0.33)	—	4.35
94.0 (73.3)	UV (C)	<sup>c</sup> (30)	26.5 (14.2)	4.03 (1.51)	3.66 (0.10)	31.7
62.2 (32.0)	$\gamma\text{-}^{60}\text{Co}$ —	20 (3.82)	0.55 (0.68)	0.36 —	—	1.80

<sup>a</sup> Approx. 5% content of *II*; <sup>b</sup> approx. 5% content of *X*; <sup>c</sup> the temperature was not measured.

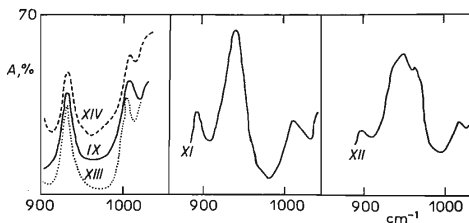


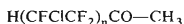
FIG. 1

IR Spectra ( $900\text{--}1040\text{ cm}^{-1}$ ) of Fluorochloroalkanols *IX* and *XI*–*XIV*

The position of the absorption bands is diminished by 10% for alcohol *XIII* and increased by 10% for alcohol *XIV*.

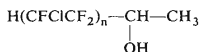
The degree of reduction of the C—Cl bonds in fluorochloroalkanol obtained from the addition of 2-butanol to trifluorochloroethylene may be followed in the IR spectra, similarly as in the case of alcohols formed on addition of 2-propanol<sup>1,7</sup>. In all alcohols which have only one atom of chlorine in the terminal —CHClF group in the molecule the shape and the position of absorption bands in the 900 to 1000 cm<sup>-1</sup> region is the same (alcohols *IX*, *XIII*, and *XIV*, Fig. 1). Also in the PMR spectra of telomers and their reduction products a characteristic change in the chemical shift of the proton in the —CFClH group is manifested<sup>7</sup>. In consequence of the reduction of the electronegative chlorine atom an increased shielding of hydrogen atoms is observed which are in close proximity to the reaction center (—CFCl— → —CFH—); this is observable from the increase of their  $\tau$ -value (approx. 0.3). In addition to this signals of protons of the —CFH— group are present in the PMR spectra of the reduction products *XIII* and *XIV* (at 4.4–4.9 $\tau$ ), which have the character of a doublet of multiplets.

The structure of the isolated products was determined on the basis of elemental analysis and IR spectra (Table II), and PMR spectra (Table III). For the confirmation of the structure of the 1 : 1 adduct *IX* and of the 1 : 2 telomer *XI* we undertook their preparation by Grignard reaction from ethylmagnesium bromide and 3,3,4-trifluoro-4-chloro-2-butanone<sup>8</sup> (*XV*) or 3,3,4,5,5,6-hexafluoro-4,6-dichloro-2-hexanone<sup>8</sup> (*XVI*).



*XV*,  $n = 1$

*XVI*,  $n = 2$



*XVII*,  $n = 1$

*XVIII*,  $n = 2$

Except for the expected tertiary alcohols *IX* and *XI* we also demonstrated the formation of the secondary alcohols 3,3,4,-trifluoro-4-chloro-2-butanol (*XVII*) and 3,3,4,5,5,6-hexafluoro-4,6-dichloro-2-hexanol (*XVIII*), which were identical with the products from the radically initiated addition of ethanol to trifluorochloroethylene<sup>8</sup>. The reductive activity of ethylmagnesium bromide was also observed in several instances where fluorinated carbonyl compounds<sup>9</sup> reacted, and they may be explained not only by sterical considerations, but also by an increased electron deficit on the oxo-group carbon atom, in consequence of the binding with the electronegative fluorochloroalkyl group<sup>10</sup>.

The addition of 2-propanol and 2-butanol initiated by <sup>60</sup>Co  $\gamma$ -radiation enabled us to carry out both additions under very similar conditions (volume of the reaction mixture, molar ratio of alcohol and olefin, time of irradiation, temperature). From the comparison of both experiments it is evident that 2-propanol is more reactive than 2-butanol.

TABLE II  
Elemental Analyses and the IR Spectra of Alcohols IX and XI—XIV

Substance (b.p., °C/Torr)	Formula (m. w.)	Calculated/Found				IR spectrum
		% C	% H	% Cl	% F	
IX (62/12)	C <sub>6</sub> H <sub>10</sub> ClF <sub>3</sub> O (190.6)	37.81	5.29	18.60	29.90	823 ms, 866 ms, 933 ms, 1010 ms, 1035 ms, 1052 s, 1080 vs, 1100 vs, 1110 vs, sh, 1138 s, sh, 1176 s, 1235 ms, 1280 ms, 1340 w, 1357 ms, 1388 ms, 1392 ms, 1467 ms, 2894 s, 2955 vs, 2990 vs, 3465 vs, 3605 vs
		38.21	5.34	18.85	29.99	
XI (100—101/12)	C <sub>8</sub> H <sub>10</sub> Cl <sub>2</sub> F <sub>6</sub> O (307.1)	31.29	3.28	23.09	37.12	835 ms, 893 ms, 940 s, 1010 ms, 1046 ms, 1073 ms, 1093 vs, sh, 1100 vs, 1144 vs, 1177 s, 1230 ms, 1245 ms, sh, 1283 ms, 1355 ms, 1393 ms, 1470 ms, 2893 s, 2955 s, 2990 vs, 3480 vs, 3610 s
		31.37	3.25	23.33	37.54	
XII <sup>a</sup> (135—137/12)	C <sub>10</sub> H <sub>10</sub> Cl <sub>3</sub> F <sub>9</sub> O (423.5)	28.36	2.38	25.11	40.37	810s,855ms,898ms,950s,963s, 1015 ms, 1050 ms, sh, 1080s,sh, 1100 vs, 1110 vs, sh, 1140 vs, 1165 vs, sh, 1230s,sh, 1275 ms, sh, 1350 ms, 1388 ms, 1392 ms, 1462 w, 1466 w, 2890 ms, 2953s, 2990s, 3470s, 3607 s
		28.81	2.48	23.83	41.37	
XIII (86—89/11)	C <sub>8</sub> H <sub>11</sub> ClF <sub>6</sub> O (272.6)	35.25	4.07	13.00	41.81	820ms, 835ms, 857s, 877ms, 933ms, 1008ms, 1030s,sh, 1055s,1080vs,1110vs,1115vs, 1145 vs, 1180 vs, 1204 vs, 1235 s, 1253 s, 1280 ms, 1357 ms, 1390 s, 1470 ms, 2894 s, 2953 vs, 2990 vs, 3470 vs, 3610 vs
		36.10	4.15	13.23	42.20	
XIV (111—113/11)	C <sub>10</sub> H <sub>12</sub> ClF <sub>9</sub> O (354.6)	33.87	3.41	10.00	48.21	836s, 864ms, 932ms, 1010ms, 1030s,sh 1045s,sh, 1083 vs, 1094 vs, 1100 vs, 1125 vs, sh, 1145 vs, sh, 1180 vs, 1200 vs, 1240 s, 1250 s, 1353 ms, 1370 ms, 1393 s, 1468 ms, 2892 s, 2953 s, 2990 vs, 3465 s, 3610 s
		34.11	3.40	10.94	47.96	

<sup>a</sup> The sample contained 20% of impurities.

TABLE III  
PMR Spectra of Fluorochloroalkanols IX and XI–XIV

Proton	IX	XI	XII	XIII	XIV
H—CFCl	3.56 (2 dt) <sup>a</sup>	3.34 (2 dt)	3.49 (2 m)	3.67 (2 m)	3.75 (2 m)
H—CF	—	—	—	4.64 (2 m)	4.87 (2 m)
CH <sub>3</sub>	8.68 (bs)	8.58 (bs)	8.62 (bs)	8.68 (s)	8.68 (s)
CH <sub>3</sub> CH <sub>2</sub>	9.02 (t)	8.99 (t)	9.00 (t)	9.01 (t)	9.00 (t)
	8.34 (q)	8.23 (q)	8.36 (q)	8.32 (q)	8.38 (q)
OH	7.61 (s)	8.07 (s)	8.27 (s)	8.00 (s)	8.11 (s)
<sup>2</sup> J <sub>HF</sub>	47.5 <sup>b</sup>	47.5	47.5	48.0	47.5
<sup>3</sup> J <sub>HF</sub>	14.8; 1.5	13.5; 2.4	—	—	—
J <sub>CH<sub>3</sub>CH<sub>2</sub></sub>	7.4	7.3	7.3	6.7	6.3

<sup>a</sup> Multiplicity of signals: bs broad singlet, t triplet, q quartet, s singlet 2 m two equal multiplets separated by <sup>2</sup>J<sub>HF</sub>, 2 dt a pair of doublets of triplets; signal values are in  $\tau$  units; <sup>b</sup> the coupling constants are in Hz units.

## EXPERIMENTAL

The temperature data are not corrected. The IR spectra were measured in tetrachloromethane on a UR-10, Zeiss, Jena spectrophotometer in the 800–2000 cm<sup>-1</sup> region. Liquid samples were measured in the 2600–3700 cm<sup>-1</sup> region. The PMR spectra were also measured in tetrachloromethane on a Tesla BS 477 (60 MHz) apparatus, using hexamethyldisiloxane as internal standard. The mass spectra were taken with a Gas Chromatograph-Mass Spectrometer LKB 9000. Gas chromatographic analyses were carried out on a Chrom II apparatus, using FID. Preparative gas chromatography was carried out on an apparatus of non-commercial origin. In both cases poly(propylene sebacate) on Celite 545 was used as stationary phase; nitrogen was the carrier gas.

### Addition Reactions

A) *Initiation by UV radiation in a flowing system at the boiling point of the alcohol:* into 100 ml (79 g) of 2-propanol in a quartz ampoule provided with a reflux condenser trifluorochloroethylene was introduced through a sintered glass filter from a pressure bottle for 9 hours at a 1.9 l/h rate. The ampoule was irradiated with a 700 W high-pressure mercury lamp, from a 5 cm distance.

B) *In a flowing system at approximately 20°C:* alcohol was poured into a glass reactor of approx. 100 ml effective volume, provided with a reflux condenser and a sintered glass filter tube for the introduction of the olefin and an immersed water-cooled high-pressure mercury lamp (Tesla RVK 125 W, quartz filter), and trifluorochloroethylene was introduced into it while the flow rate was measured with a flow-meter. The temperature of the reaction mixture was maintained at 20–30°C by cooling the lamp with water.

C) *In a closed system under increased pressure:* Into a 250 ml quartz ampoule 94.0 g (1.27 mol) of 2-butanol were poured, the ampoule was rinsed with nitrogen, evacuated with a water-pump, and cooled in a mixture of solid carbon dioxide and ethanol. Trifluorochloroethylene (73.3 g; 0.63 mol) dried with anhydron was then condensed into the ampoule. The latter was sealed and irradiated with a high-pressure Tesla RVK 400 W mercury lamp from a 7 cm distance for 30

hours. The ampoule was then cooled, opened, and the unreacted olefin was evaporated from a 40°C warm bath.

D) *Initiation with  $^{60}\text{Co}$   $\gamma$ -radiation*: The additions were carried out in glass ampoules of approx. 150 ml volume. The filling of ampoules with the reaction mixture and their opening was the same as in procedure C. The reaction mixture was exposed to  $^{60}\text{Co}$   $\gamma$ -radiation of 391. 913 r/hour intensity for 3 hours 49 minutes.

#### Working up of the Reaction Mixtures

Reaction mixtures were fractionated under reduced pressure. All fractions were analysed gas chromatographically. From these data total amounts of single products were computed. The weights of starting components, reaction conditions, and the results of the addition of alcohols are given in Table I.

#### Addition of 2-Propanol to Trifluorochloroethylene

From the addition initiated according to B 57.5 g of a fraction boiling at 145–147°C, 22.5 of a fraction boiling at 44–110°C/10 Torr, 7.2 g of a fraction boiling at 110–141°C/10 Torr, and 7.5 g of the distillation residue were obtained. Alcohols I and III–VIII were identified by gas chromatography by comparison with standard, while alcohol I was also identified on the basis of its IR spectrum (comparison with a standard). The structure of alcohol II is derived from its mass spectrum.

#### Addition of 2-Butanol to Trifluorochloroethylene

From the addition initiated according to C the following fractions were obtained: 1. 16.8g of fraction b.p. 60–66°C/12 Torr, which according to gas chromatography consisted of 88% of alcohol IX. Further rectification gave chromatographically pure 1 : 1 adduct IX, b.p. 62°C/12 Torr, accompanied by approx. 5% of alcohol X the structure of which was determined on the basis of its mass spectrum; 2. 12.6 g of fraction b.p. 98–110°C/12 Torr the rectification of which gave chromatographically pure 1 : 2 telomer XI, b.p. 100–101°C/12 Torr; 3. 8.7 g of fraction b.p. 135–146°C/12 Torr from which a product was obtained on double rectification, that was 80% pure, b.p. 135–137°C/12 Torr. The main component of this fraction was identified as 1 : 3 telomer XII.

#### Reduction of C—Cl Bonds in Alcohols XI and XII

*Telomer XI*: A solution of 4.7 g of alcohol XI in 25 ml of 2-propanol was placed in a quartz test tube of 30 ml volume, fitted with a reflux condenser, and irradiated externally with a high-pressure mercury lamp Tesla RVK 400 W for 16 hours. After the distillation off of the excess 2-propanol and rectification of the residue 2.6 g of a substance were obtained, b.p. 87–89°C/11 Torr which was identified as alcohol XIII. It was demonstrated gas chromatographically that it is identical with the substance accompanying alcohol XI in the reaction mixture after addition.

*Telomer XII*: A solution of 9.6 g of alcohol XII in 50 ml of 2-propanol was irradiated in a quartz tube for 27 hours under the same conditions as in the preceding experiment. After the evaporation of 2-propanol the dark residue was diluted with ether, the solution was washed with aqueous sodium hydrogen carbonate, and dried over sodium sulfate. After filtration and evaporation of ether it was submitted to fractional distillation. Yield 4.3 g of a product, b.p. 111 to 113°C/11 Torr, which according to gas chromatographic analysis contained 10% of an unidentified substance



with shorter elution time, which was identified as alcohol *XIV*. This alcohol was chromatographically identical with one of the three substances (with shortest time) which accompanied alcohol *XIII* in the reaction mixture after addition.

#### Reaction of Ketones *XV* and *XVI* with Ethylmagnesium Bromide

*Ketone XV*: To an ethereal solution of ethylmagnesium bromide in 15 ml of ether, prepared from 4.9 g of ethyl bromide and 1.1 g of magnesium spans, a solution of ketone *XV* (7.2 g) in 10 ml of ether was added dropwise and boiled for 10 minutes. The mixture was decomposed with dilute sulfuric acid and the ethereal layer was separated and the aqueous layer was extracted twice with ether. The combined ethereal layers were washed with a sodium hydrogen carbonate solution and then dried over magnesium sulfate. Ether was distilled off and the residue distilled to give 4 g of a product, b.p. 47–60°C/11 Torr, which according to gas chromatography contained two main components in a 2 : 3 relative ratio. Both substances were separated by preparative gas chromatography. The first component, having a shorter elution time, was identified as 3,3,4-trifluoro-4-chloro-2-butanol by comparison of its chromatographic behavior, IR and PMR spectra with a standard. The substance with a longer elution time was identified as alcohol *IX* by an analogous comparison with the 1 : 1 adduct *IX* from the addition of 2-butanol.

*Ketone XVI*: An analogous reaction, starting from 6.2 g of ketone *XVI*, 2.5 g of ethyl bromide, and 0.55 g of magnesium, and worked up as above, gave 3.05 g of a fraction, b.p. 75–82°C/10 Torr, which according to gas chromatographic analysis contained in addition to some unidentified substances alcohols *XVIII* and *XI* in a relative 9 : 2 ratio. The alcohols were identified by the comparison of their elution times with the standards from the addition of ethanol and 2-butanol to trifluorochloroethylene.

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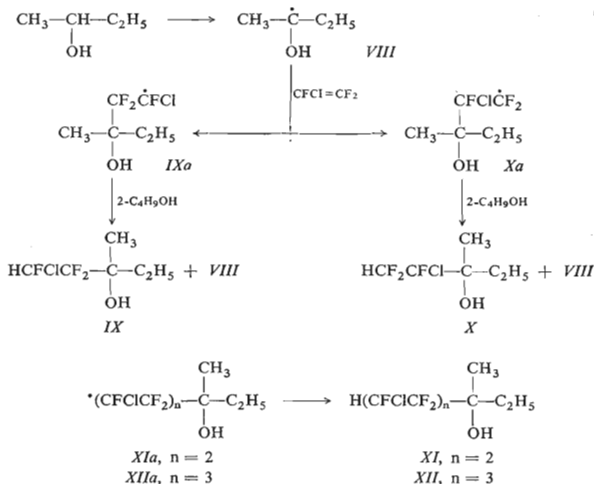
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Translated by Ž. Procházka.

CHEMISTRY OF ORGANIC FLUORINE COMPOUNDS. XIII.  
 RADICALIC ADDITION OF 2-PROPANOL AND 2-BUTANOL TO  
 TRIFLUOROCHLOROETHYLENE

F. LIŠKA, M. NĚMEC and V. DĚDEK

This Journal 37, 2091 (1972). The following Scheme 2 was omitted:



SCHEME 2

ALKALOIDS OF THE *Papaveraceae*. XLVII.  
 IDENTITY OF BOCCONINE WITH CHELIRUBINE

J. SLAVÍK and F. ŠANTAVÝ

This Journal 37, 2805, 2806 (1972). p. 2805, 2nd paragraph should read: On the contrary, substitution by two electron ... P. 2806, reference 9. should read: This Journal 37, 2746 (1972).