RADICAL ADDITION OF SECONDARY ALCOHOLS TO TRIFLUOROCHLOROETHYLENE AND CYCLISATION OF FLUOROCHLOROALKANOLS UNDER THE FORMATION OF FLUORINATED OXETANES AND TETRAHYDROPYRANS*

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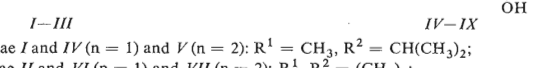
The tertiary alcohols obtained by the photochemically and γ-^{60}Co initiated addition of 3-methyl-2-butanol, cyclopentanol, and cyclohexanol to trifluorochloroethylene, were cyclised to fluorinated cyclic ethers by the action of aqueous sodium hydroxide. The cyclisation is accompanied by intramolecular substitution of the chloro atom in the CHClF group. The 1 : 1 adducts afforded fluorinated oxetanes while fluorinated tetrahydropyrans (oxanes) were obtained from 1 : 2 telomers.

In connection with investigations on the synthetic utilisation of trifluorochloroethylene in radical addition reactions, the addition and telomeric products from additions of primary and secondary alcohols to trifluorochloroethylene have been observed to undergo cyclisation in alkali under the formation of fluorinated derivatives of oxetane and tetrahydropyran[1,2]. In the present paper, we wish to report the preparation of some additional fluorinated oxetanes and tetrahydropyrans by the intramolecular cyclisation of fluorochloroalkanols obtained from radical additions of 2-butanol[3], 3-methyl-2-butanol (*I*), cyclopentanol (*II*), and cyclohexanol (*III*) to trifluorochloroethylene. The addition of alcohols *I*–*III* to trifluorochloroethylene was initiated by the ultraviolet radiation and also by the ^{60}Co γ-radiation. For the reaction conditions and yields of particular experiments see Table I.



I–*III* *IV*–*IX*

In formulae *I* and *IV* (n = 1) and *V* (n = 2): $R^1 = CH_3$, $R^2 = CH(CH_3)_2$;
in formulae *II* and *VI* (n = 1) and *VII* (n = 2); $R^1, R^2 = (CH_2)_4$;
in formulae *III* and *VIII* (n = 1) and *IX* (n = 2): $R^1, R^2 = (CH_2)_5$.

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By the addition to trifluorochloroethylene, 3-methyl-2-butanol (*I*) afforded 3,4-dimethyl-1,2,2-trifluoro-1-chloro-3-pentanol (*IV*) and 2,3-dimethyl-4,4,5,6,6,7-hexafluoro-5,7-dichloro-3-heptanol (*V*); cyclopentanol (*II*) gave 1-(1,1,2-trifluoro-2-chloroethyl)cyclopentanol (*VI*) and 1-(1,1,2,3,3,4-hexafluoro-2,4-dichlorobutyl)cyclopentanol (*VII*); and cyclohexanol (*III*) furnished 1-(1,1,2-trifluoro-2-chloroethyl)cyclohexanol (*VIII*) and 1-(1,1,2,3,3,4-hexafluoro-2,4-dichlorobutyl)cyclohexanol (*IX*). The 1 : 1 adducts *IV*, *VI*, and *VIII*, and the telomers *V*, *VII*, and *IX* were isolated from the reaction mixture by rectification. The particular interfractions were shown by gas chromatography to contain some additional compounds which, however, were not isolated and identified because of the small quantity available. It may be assumed on the basis of earlier findings that these compounds represent products of the reduction of C—Cl bonds in 1 : 2 telomers[4] or products formed by trifluorochloroethylation at β-carbon atoms[5]. The structure of alcohols *IV*–*IX* was determined by elemental analysis (Table II), IR spectra (alcohol, $\nu(OH)_{bound}$ and $\nu(OH)_{free}$ in cm^{-1}; *IV*, 3480 and 3604; *V*, 3490 and 3618; *VI*, 3465 and 3605; *VII*, 3470 and 3610; *VIII*, 3470 and 3602; and *IX*, 3480 and 3610), and NMR spectra (Table III). The NMR spectra of alcohols *IV*–*IX* exhibit a characteristic change in the

TABLE I

Addition of Alcohols $R^1CH(OH)R^2$ to Trifluorochloroethylene

R^1, R^2 Method, g	$CFCl{=}CF_2$ g (l/h)	Temperature, °C (time in h)	Reaction products g		Distillation residue g
CH_3, $CH(CH_3)_2$			*IV*	*V*	
A, 82·0	115·0 (1·1)	50 (22)	9·35	1·22	6·5
B, 104·0	75·2	*a* (39)	12·70	3·98	41·2
C, 65·2	27·2	20 (3·82)	0·22	0·24	0·60
$(CH_2)_4$			*VI*	*VII*	
A, 93·2	52·5 (1·0)	20 (11)	16·49	2·14	7·2
B, 116·3	87·7	*a* (39)	19·30	8·80	44·8
C, 73·2	34·2	20 (3·82)	2·37	1·85	3·9
$(CH_2)_5$			*VIII*	*IX*	
A, 96·2	143·0 (1·0)	60 (30)	19·76	0·66	4·0
B, 112·2	103·0	*a* (47)	15·00	10·60	70·0
C, 74·8	29·6	20 (3·82)	1·91	1·07	2·8

[a] The temperature was not measured.

chemical shift of the proton in the FCHCl group with the 1 : 1 adducts *IV*, *VI*, and *VIII*, and with the 1 : 2 telomers *V*, *VII*, and *IX*. In the latter case of the 1 : 2 telomers *V*, *VII*, and *IX*, the chemical shift is decreased by about 0·2δ (*cf.*[4]). Furthermore, in alcohols *VI* and *VIII* the proton of the FCHCl group is split by geminal and vicinal interactions with fluorine atoms to a doublet of doublets doublet (ddd). This splitting is characteristic of compounds of the H—$CFClCF_2$—R type with one chirality

TABLE II

Elemental Analyses and Boiling Points of Alcohols *IV*—*IX*, Oxetanes *X*—*XII*, and Tetrahydropyrans *XIV*—*XVI*

Compound (b.p., °C/Torr)	Formula (m.w.)	Calculated/Found			
		% C	% H	% Cl	% F
IV	$C_7H_{12}ClF_3O$	41·09	5·91	17·33	27·85
(66—67/11)	(204·6)	41·40	5·91	17·63	27·75
V	$C_9H_{12}Cl_2F_6O$	33·67	3·77	22·08	35·50
	(321·1)	33·74	3·83	21·86	35·62
VI	$C_7H_{10}ClF_3O$	41·50	4·98	17·50	28·13
(80/11)	(202·6)	41·56	4·93	17·63	28·22
VII	$C_9H_{10}Cl_2F_6O$	33·88	3·16	22·22	35·73
(116—118/11)	(319·1)	34·08	3·31	22·06	35·49
VIII	$C_8H_{12}ClF_3O$	44·36	5·58	16·37	26·31
(93/11)	(216·6)	44·87	5·63	16·41	26·35
IX[a]	$C_{10}H_{12}Cl_2F_6O$	36·06	3·63	21·29	34·22
(123—126/11)	(333·1)	37·94	4·09	20·16	32·01
X	$C_7H_{11}F_3O$	50·00	6·59	—	33·89
(107—109)	(168·2)	50·30	6·67	—	33·66
XI	$C_7H_9F_3O$	50·61	5·46	—	34·30
(120—121)	(166·1)	50·64	5·49	—	34·18
XII	$C_8H_{11}F_3O$	53·33	6·15	—	31·63
(133—136)	(180·2)	53·26	6·27	—	31·67
XIV	$C_8H_9ClF_6O$	35·51	3·35	13·10	42·12
(51—55/11)	(270·6)	35·66	3·35	13·38	42·51
XV	$C_9H_9ClF_6O$	38·25	3·21	12·54	40·33
	(282·6)	38·65	3·35	12·83	40·41
XVI	$C_{10}H_{11}ClF_6O$	40·49	3·74	11·95	38·43
(113—115/45)	(296·6)	40·85	3·89	12·12	39·45

[a] The sample contained about 20% of contaminants.

TABLE III

NMR Spectra of Fluorochloroalkanols *IV*–*IX*

Proton[a]	*IV*	*V*	*VI*	*VII*	*VIII*	*IX*
HCFCl	6·46 ddm	6·64 ddm	6·47 ddd	6·68 ddm	6·45 ddd	6·64 ddt
CH_3	1·27 s	1·34 s	—	—	—	—
CH	2·05 m	2·23 m	—	—	—	—
$(CH_3)_2$	1·00 d	1·04 d	—	—	—	—
$(CH_2)_n$	—	—	1·81 s	1·85 s	1·66 s	1·70 s
OH	1·85 s	1·85 s	2·14 s	1·99 s	1·83 s	2·04 s
$^2J_{HF}$	47·3	47·5	48·0	47·0	48·0	47·5
$^3J_{HF}$	13·5	13·0	14·0	13·0	14·4	13·5
			2·4		1·5	1·7
$^3J_{HH}$	6·8	6·8	—	—	—	—

[a] Shift values δ in p.p.m., J in Hz.

center in the molecule when, *e.g.*, R equal to —C(OH)$(CH_3)_2$ (*cf.*[2,4]), —CH_2N.$(CH_3)_2$ (*cf.*[6]), —CH_2N(CH_3)CH$(CH_3)_2$ (*cf.*[7]), —CH$(OCH_2)_2$ (*cf.*[8]), —$COCH_3$ (*cf.*[5]), and $CFCl_2$ (*cf.*[9]). An exception is formed by compounds where R designates a less bulky grouping of atoms such as —CH_2OH (*cf.*[10]) or —CH_2Cl (*cf.*[11]); with the corresponding compounds, the proton signal of the FCHCl group manifests itself in the shape of the assumed doublet of triplets (dt). Owing to the presence of two

TABLE IV

NMR Spectra of Fluorinated Oxetanes *X*–*XII* and Tetrahydropyrans *XIV*–*XVI*

Proton[a]	*X*	*XI*	*XII*	*XIV*	*XV*	*XVI*
CHF	5·75 dm	5·77 dm	5·76 dm	5·61 dm	5·60 dm	5·63 dm
CH	2·29 m	—	—	—	—	—
CH_3	1·28 d[b]	—	—	1·50 s	—	—
	1·39 d[b]					
$(CH_3)_2$	0·92 d	—	—	—	—	—
	0·99 d					
CH_3CH_2	—	—	—	1·04 t	—	—
CH_2	—	1·83 m	1·69 m	1·84 q	1·87 s	1·62 s
$^2J_{HF}$	69·3	69·7	67·0	50·2	51·0	51·0
$^3J_{HH}$	7·0	—	—	7·3	—	—

[a] Shift values δ in p.p.m., J in Hz; [b] $J = 2{\cdot}5$ Hz.

chirality centers, the alcohol *IV* is a mixture of two diastereoisomeric racemates, the resolution of which by gas chromatography failed. Concerning the NMR spectrum, the attempted assignment of the chemical shift signals for the FCHCl group to particular diastereoisomers was also unsuccessful; doublet of multiplets is therefore given. Similarly in the case of 1 : 2 telomers *V*, *VII*, and *IX* and the structurally related alcohols[2-4], the proton signal in the FCHCl group manifests itself as a doublet of triplets dublet or as a doublet of multiplets doublet.

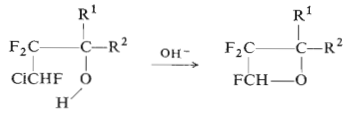
An earlier paper[2] reports the preparation of fluorinated derivatives of oxetane and tetrahydropyran by an alkaline cyclisation of fluorochloroalkanols according to the general formula $H—(CFClCF_2)_nC(OH)R^1R^2$ wherein n is equal to one or two. Also in the present work, the addition and telomeric products were processed with aqueous sodium hydroxide. Thus, the 1 : 1 adducts afforded fluorinated derivatives of oxetane, namely, 2-methyl-2-isopropyl-3,3,4-trifluorooxetane (*X*) from the alcohol *IV*, 3-oxa-1,1,2-trifluorospiro[3.4]octane (*XI*) from the alcohol *VI*, and 3-oxa--1,1,2-trifluorospiro[3.5]nonane (*XII*) from the alcohol *VIII*.

The cyclisation of 1 : 2 telomers afforded fluorinated tetrahydropyrans (oxanes) such as 2-methyl-2-ethyl-3,3,4,5,5,6-hexafluoro-4-chlorotetrahydropyran (*XIV*) from 3-methyl-4,4,5,6,6,7-hexafluoro-5,7-dichloro-3-heptanol[3] (*XIII*), 10-oxa-6,6,7,8,8,9--hexafluoro-7-chlorospiro[4.5]decane (*XV*) from the alcohol *VII*, and 5-oxa--1,1,2,3,3,4-hexafluoro-2-chlorospiro[5.5]undecane (*XVI*) from the alcohol *IX*.

TABLE V

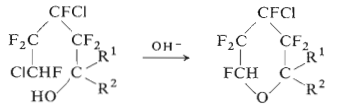
Reaction Conditions and Products of the Cyclisation of Fluorochloroalkanols *IV*, *VI—IX*, and *XIII*

Alcohol g (mmol)	NaOH, g (mmol) H_2O, ml	Time, h	Product g (mmol,) %
IV 12·6 (61)	12·0 (300) 30	22	*X* 9·8 (58), 95·0
VI 6·0 (30)	6·0 (150) 15	12	*XI* 4·0 (24), 80·0
VIII 12·2 (56)	11·2 (280) 30	12	*XII* 7·3 (41), 73·0
XIII 11·3 (37)	10·0 (250) 30	16	*XIV* 4·3 (16), 43·5
VII 2·25 (7)	2·0 (50) 5	17	*XV* 1·1 (4), 55·6
IX 5·5 (16)	6·0 (150) 15	18	*XVI* 3·8 (13), 81·0



IV, VI, VIII *X, XI, XII*

In formulae *IV* and *X*: $R^1 = CH_3$, $R^2 = CH(CH_3)_2$;
in formulae *VI* and *XI*: $R^1, R^2 = (CH_2)_4$;
in formulae *VIII* and *XII*: $R^1, R^2 = (CH_2)_5$.



VII, IX, XIII *XIV–XVI*

In formulae *XIII* and *XIV*: $R^1 = CH_3$, $R^2 = C_2H_5$;
in formulae *VII* and *XV*: $R^1, R^2 = (CH_2)_4$;
in formulae *IX* and *XVI*: $R^1, R^2 = (CH_2)_5$.

The structure of oxetanes and tetrahydropyrans was determined on the basis of elemental analysis (Table II) and NMR spectra (Table III and IV). The oxetane *X* and tetrahydropyrans *XV* and *XVI* represent a mixture of two diastereoisomeric racemates[2] as demonstrated by gas chromatography (*XV* and *XVI*); the isolation in a pure state was not effected. In the case of the oxetane *X*, the presence of racemates may be inferred only on the basis of methyl groups signals in NMR spectrum. Since the molecule of the tetrahydropyran *XIV* possesses three chirality centers, four diastereoisomeric racemates may be expected; their presence was confirmed by gas chromatography and the components were identified simultaneously as the whole mixture.

EXPERIMENTAL

The boiling points are uncorrected. The IR spectra were taken on a UR-10 Zeiss Jena apparatus. The NMR spectra were recorded on Tesla 477 (60 MHz) and Tesla 478 (80 MHz) apparatus in tetrachloromethane or deuteriochloroform. The gas-chromatographical analyses were performed on a Chrom 11 apparatus (Czechoslovakia) with flame ionisation detection. Unless stated otherwise, 20% polypropylene sebacate on Cellite 545 was used as the stationary phase (nitrogen as carrier gas).

Chemicals

The commercially available trifluorochloroethylene was used as produced by the Society for Chemical and Metallurgical Production, Ústí nad Labem, Czechoslovakia. 3-Methyl-2-butanol (*I*) was prepared from isopropylmagnesium bromide and acetaldehyde in 54% yield[12]. Cyclopentanol (*II*) was obtained by the lithium aluminium hydride reduction of cyclopentanone in 66% yield[13].

Radical Addition of Alcohols *I*—*III* to Trifluorochloroethylene

The additions of alcohols *I*—*III* were performed under initiation with ultraviolet radiation by introduction of trifluorochloroethylene into the corresponding secondary alcohol (method *A*), by irradiation of a solution of the alcohol and trifluorochloroethylene in a sealed quartz ampoule (method *B*), or by initiation with the ^{60}Co γ-radiation in a glass ampoule. For the experimental technique and processing of reaction mixtures see an earlier paper[3]. The reaction conditions and results are summarised in Table I. The total amount of products given in Table I represents a sum of products obtained by distillation and contained in interfractions (as calculated from chromatograms of these interfractions). For the elemental analyses see Table II, for NMR spectra of alcohols see Table III.

Preparation of Oxetanes *X*—*XII*

Emulsions of alcohols *IV*, *VI* and *VIII* in aqueous sodium hydroxide were refluxed under efficient stirring, diluted with water, and subjected to distillation under continuous stirring. The aqueous layer of the distillate was discarded while the oil was dried over anhydrous magnesium sulfate and distilled. For the amounts of reactants, reaction conditions, and results see Table V. The elemental analyses are given in Table II and the NMR spectra in Table IV.

Preparation of Tetrahydropyrans *XIV*—*XVI*

Emulsions of alcohols *XIII*, *VII*, and *IX* in aqueous sodium hydroxide were processed analogously to the preparation of oxetanes. As shown by the gas-chromatographical analysis (polypropylene sebacate on Cellite, 80°C), the tetrahydropyrans *XV* and *XVI* are formed by pairs of diestereoisomers which were not separated and were identified as the whole. The analysis (performed under similar conditions) of *XIV* indicated the presence of only three compounds in the ratio 2 : 1 : 1 (elution distances, 120 mm, 170 mm, and 190 mm). The complete separation of the four diastereoisomers of the tetrahydropyran *XIV* was effected on a 50 m capillary column (dinonyl phthalate); the preparative separation was not performed. For the amounts of reactants, reaction conditions, and results see Table V. The elemental analyses are given in Table II and the NMR spectra in Table IV.

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