SYNTHESIS OF FLUOROCHLOROALKANOLS AND THEIR CYCLISATION TO FLUORINATED OXOLANES*

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4-Chloro-3,3,4-trifluoro-2-methyl-1-butene (*VI*) and 4-chloro-3,3,4-trifluoro-1-butene (*XXIX*) were transformed by hydroboration, addition of hypochlorous acid and hydroxylation of the double bond into alcohols with 2-chloro-1,1,2-trifluoroethyl group in β-position relative to the hydroxyl group. These alcohols on reaction with aqueous or ethanolic sodium or potassium hydroxide undergo cyclisation to the corresponding derivatives of 2,3,3-trifluorooxolane.
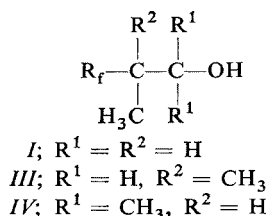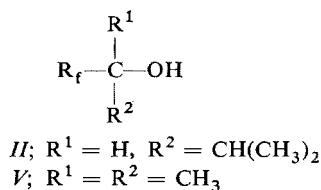
In our previous studies[1,2] we have found that secondary and tertiary fluorochloro-alkanols of the general formula $H(CFClCF_2)_nC(OH)R^1R^2$, where $n = 1$ or 2 and R^1, $R^2 = H$ or alkyl, are dehydrochlorinated in an alkaline medium to give fluoro derivatives of oxetane and oxane (tetrahydropyran). This reaction is a nucleophilic substitution of the chloro atom in the terminal CHClF group placed in β or δ position relative to the hydroxyl-bearing carbon. The objective of this paper was to synthesize in an analogous way fluorinated oxolane derivatives, hitherto available only by a direct fluorination of oxolane and its derivatives[3–5], or by cyclodehydration of fluorinated 1,4-butanediols[6]. Formation of oxolanes was also noted in the electrofluorination of aliphatic acids[7]. To this end, we worked out syntheses of fluorochloroalkanols, having the CHClF group in a γ-position relative to the hydroxyl-substituted carbon. The first alcohol of this type, identified by us among the products of the radical addition of 1-propanol to trifluorochloroethylene, was 4-chloro-3,3,4-trifluoro-2-methyl-1-butanol (*I*) which was the product of trifluoroethylation reaction on the β-carbon atom[8].

In the present study we made use of this finding and carried out the addition of 2--methyl-1-propanol to trifluorochloroethylene, expecting a greater yield of β-trifluorochloro derivative as compared with the addition of 1-propanol.

The reaction of 2-methyl-1-propanol with trifluorochloroethylene, initiated by the UV radiation, afforded a mixture of 1 : 1 adducts, consisting of 1-chloro-1,2,2-tri-
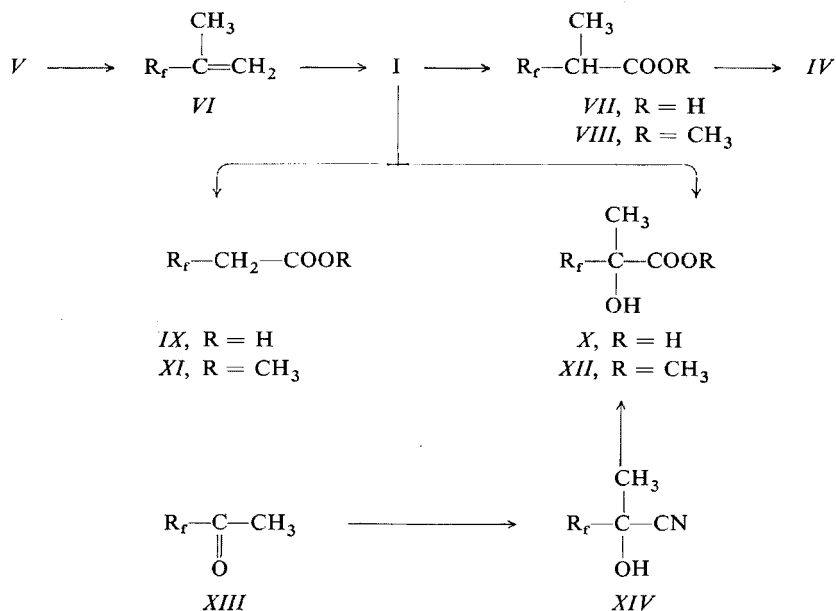
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fluoro-4-methyl-3-pentanol (II) and 4-chloro-3,3,4-trifluoro-2,2-dimethyl-1-butanol (III) in the ratio 2·6 : 1.

$$R_f\text{—}\underset{\underset{R^2}{|}}{\overset{\overset{R^1}{|}}{C}}\text{—OH} \qquad\qquad R_f\text{—}\underset{\underset{H_3C}{|}}{\overset{\overset{R^2}{|}}{C}}\text{—}\underset{\underset{R^1}{|}}{\overset{\overset{R^1}{|}}{C}}\text{—OH}$$

II; $R^1 = H$, $R^2 = CH(CH_3)_2$ I; $R^1 = R^2 = H$
V; $R^1 = R^2 = CH_3$ III; $R^1 = H$, $R^2 = CH_3$
               IV; $R^1 = CH_3$, $R^2 = H$

In the formulae $I - V$ $R_f = CHClFCF_2$—

Other alcohols with trifluorochloroethyl group attached to the β carbon atom, prepared by us in the present study, are 4-chloro-3,3,4-trifluoro-2-methyl-1-butanol (I) and 5-chloro-4,4,5-trifluoro-2,3-dimethyl-2-pentanol (IV). We synthesized these compounds starting from 4-chloro-3,3,4-trifluoro-2-methyl-2-butanol[9,10] (V) which was dehydrated by phosphorus pentoxide[9] or thionyl chloride to 4-chloro-3,3,4-trifluoro-2-methyl-1-butene (VI). Hydroboration of the olefin VI afforded butanol I; this method of preparation is superior to the radical addition of 1-propanol to trifluorochloroethylene[8]. The alcohol I served then as the starting material for the

$$V \longrightarrow R_f\text{—}\underset{\underset{VI}{}}{\overset{\overset{CH_3}{|}}{C}}\text{=}CH_2 \longrightarrow I \longrightarrow R_f\text{—}\overset{\overset{CH_3}{|}}{CH}\text{—}COOR \longrightarrow IV$$

                  VII, $R = H$
                 $VIII$, $R = CH_3$

$$R_f\text{—}CH_2\text{—}COOR \qquad\qquad R_f\text{—}\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}\text{—}COOR$$

IX, $R = H$ X, $R = H$
XI, $R = CH_3$ XII, $R = CH_3$

$$R_f\text{—}\underset{\underset{O}{\|}}{C}\text{—}CH_3 \longrightarrow R_f\text{—}\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}\text{—}CN$$

$XIII$ XIV

In the formulae $VI - XIV$, $R_f = HCFClCF_2$—.

synthesis of pentanol *IV*: oxidation of *I* with chromic acid gave 4-chloro-3,3,4-tri-fluoro-2-methylbutanoic acid *(VII)*; this was converted by treatment with diazomethane into its methyl ester *VIII* which on reaction with methylmagnesium iodide afforded the pentanol *IV*.

Oxidation of the butanol *I* with dilute nitric acid is more complicated. The principal product is 4-chloro-3,3,4-trifluoro-2-hydroxy-2-methylbutanoic acid *(X)*. The acid *VII*, together with 4-chloro-3,3,4-trifluorobutanoic acid *(IX)*, are only side-products. We converted the mixture of acids *VII*, *IX* and *X* into the corresponding esters *VIII*, *XI* and *XII* by treatment with diazomethane and from the ester mixture the hydroxy ester *XII* was isolated and identified by its IR, NMR and mass spectra. Moreover, we reduced *XII* with lithium aluminium hydride to 4-chloro-3,3,4-trifluoro-2-me-thyl-1,2-butanediol *(XV)* which was identical with the diol *XV* synthesized by hydroxylation of the olefin *VI*. We prepared the ester *XII* also independently by cyanohydrin synthesis from the previously described 4-chloro-3,3,4-trifluoro-2-butanone[11] *(XIII)* *via* the corresponding 4-chloro-3,3,4-trifluoro-2-hydroxy-2-methylbutyronitrile *(XIV)*.

Another route, leading to fluorochloroalkanols with the terminal CHClF group in the γ position relative to the hydroxyl-substituted carbon, is the addition of hypochlorous acid to the olefin *VI*, using tert-butyl hypochlorite.
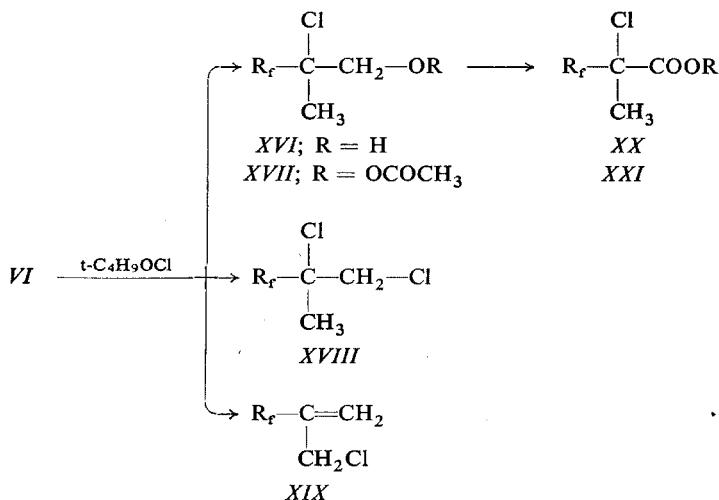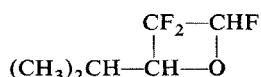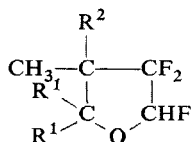

Due to the presence of the electronegative trifluorochloroethyl group in the olefin *VI*, the addition of hypochlorous acid to this olefin is considerably selective, affording as the principal product the chlorohydrin *XVI* or its acetate *XVII*. When the reaction is conducted in aqueous acetone, the main product is 2,4-dichloro-3,3,4-trifluoro--2-methylbutanol *(XVI)*, in aqueous acetic acid a mixture (13 : 87) of the butanol

XVI and the acetate *XVII* arises, whereas the reaction in anhydrous acetic acid yields only the acetate *XVII*. Among other products of these additions we identified 1,3,4--trichloro-1,2,2-trifluoro-3-methylbutane *(XVIII)* and 4-chloro-2-chloromethyl-3,3,4-trifluoro-1-butene *(XIX)*. The alcohol *XVI* and the acetate *XVII* were oxidized to 2,4-dichloro-3,3,4-trifluoro-2-methylbutanoic acid *(XX)* which was converted into its ester by treatment with diazomethane.

The alcohols *I*, *III*, *IV* and the acetate *XVII* were cyclised to fluorinated oxolanes by the reaction with aqueous sodium hydroxide at 80–90°C. Cyclisation of the mixture of alcohols *II* and *III*, obtained in the addition of 2-methyl-1-propanol to trifluorochloroethylene, afforded a mixture of 3,3,4-trifluoro-2-isopropyloxetane *(XXII)* and 2,3,3-trifluoro-4,4-dimethyloxolane *(XXIII)*, which was separated into the components by preparative gas–liquid chromatography. The reaction of the individual alcohols *I* and *IV* with aqueous sodium hydroxide gave 2,3,3-trifluoro-4-methyl-oxolane *(XXIV)* and 4,4,5-trifluoro-2,2,3-trimethyloxolane *(XXV)*, respectively.

Cyclisation of the acetate *XVII* at 80°C afforded 4-chloro-2,3,3-trifluoro-4-methyl-oxolane *(XXVI)*; when the cyclisation was carried out at 20°C, we isolated in addition to the oxolane *XXVI* also 2-methyl-2-(2-chloro-1,1,2-trifluoroethyl) oxirane *(XXVII)* as the product of competitive dehydrochlorination. The ratio of the oxolane *XXVI* to the oxirane *XXVII* was 15 : 85.

$$CF_2—CHF$$
$$(CH_3)_2CH—CH—O$$

XXII

$$\begin{array}{c} R^2 \\ CH_3—C\!-\!\!-\!CF_2 \\ R^1 \\ C\quad CHF \\ R^1 \quad O \end{array}$$

XXIII; $R^1 = H$, $R^2 = CH_3$
XXIV; $R^1 = R^2 = H$
XXV; $R^1 = CH_3$, $R^2 = H$
XXVI; $R^1 = H$, $R^2 = Cl$

$$\begin{array}{c} CH_3 \\ CHClFCF_2—C\!-\!\!-\!CH_2 \\ O \end{array}$$
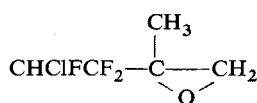
XXVII

Cyclisation of 4-chloro-3,3,4-trifluoro-2-methyl-1,2-butanediol *(XV)* and 4-chloro--3,3,4-trifluoro-1,2-butanediol *(XXVIII)* can lead to formation of oxetane or oxolane derivatives since the starting compounds contain the chlorofluoromethyl group in the β- as well as in the γ-position relative to hydroxyl. For the preparation of greater amounts of the diol *XV*, the method of choice is hydroxylation of the olefin *VI*. We used the same reaction also in the synthesis of diol *XXVIII* from 4-chloro-3,3,4-trifluoro-1-butene *(XXIX)*, which was prepared by pyrolysis of 4-chloro-3,3,4-tri-fluoro-2-butyl acetate *(XXX)*. Whereas the reaction of the tertiary alcohol *V* with thionyl chloride results in dehydration to the olefin *VI*, in the case of 4-chloro-3,3,4--trifluoro-2-butanol *(XXXI)* chlorine substitutes hydroxyl group under formation of 1,3-dichloro-1,2,2-trifluorobutane *(XXXII)*.

$$HCFClCF_2-CH-CH_3$$
$$|$$
$$OR$$

XXXI; R = H
XXX; R = COCH_3

$$HCFClCF_2-CH-CH_3$$
$$|$$
$$Cl$$
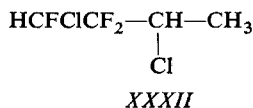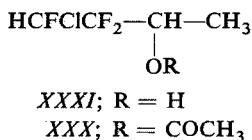
XXXII

In the cyclisation reaction of both diols *XV* and *XXVIII* in an alkaline medium we isolated only the corresponding oxolanes, *i.e.* 2,3,3-trifluoro-4-hydroxy-4-methyl-oxolane *(XXXIII)* and 2,3,3-trifluoro-4-hydroxyoxolane *(XXXIV)* without being successful in proving any oxetane *XXXV* (gas–liquid chromatography).

VI; R = CH_3   XV; R = CH_3   XXXIII; R = CH_3
XXIX; R = H   XXVIII; R = H   XXXIV; R = H
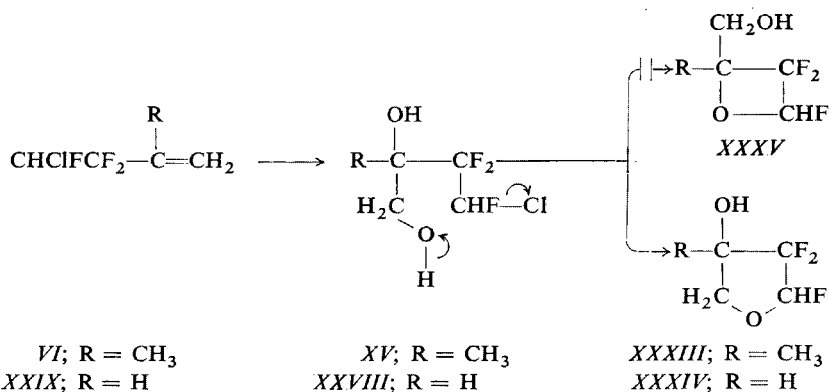
We have determined the structure of the oxolanes *XXXIII* and *XXXIV* on the basis of the magnitude of the geminal coupling constants $(^2J_{HF})$ of the hydrogen and fluorine nuclei in the NMR spectra; in this way we also eliminated the structure of the isomeric oxetanes *XXXV*. Whereas the oxetane derivatives, hitherto known by us, exhibit $^2J_{HF} \sim 68-70$ Hz and oxane derivatives[1,2] have $J \sim 48-51$ Hz, for the oxolane derivatives the value of J is in the region $62-65$ Hz (ref.[3] states $57-64$ Hz).

Since molecules of the oxolanes *XXIV–XXVI, XXXIII* and *XXXIV* contain two chiral centers, it may be anticipated that these compounds are mixtures of two diastereoisomeric racemates. In all cases we were able to prove their presence by means of gas–liquid chromatography and by the identity of their mass spectra. The diastereoisomeric racemates of *XXV, XXXIII* and *XXXIV* were isolated by preparative gas–liquid chromatography; in the case of *XXIV* the isomers were separated only on a capillary column (50 m, nonyl phthalate) and therefore they were identified as a mixture. Diastereoisomers of *XXVI* were not separated.

EXPERIMENTAL

The temperature data are uncorrected. IR spectra were taken in tetrachloromethane on UR-10, Zeiss, Jena and Perkin-Elmer 325 spectrophotometers in the region $800-2000 \text{ cm}^{-1}$ and $2600-3700 \text{ cm}^{-1}$. The NMR spectra were measured on Tesla BS 477 (60 MHz), Tesla BS 478 (80 MHz) and Varian XL 100 instruments, in tetrachloromethane or deuteriochloroform, using tetramethylsilane or hexamethyldisiloxane as internal standards. Mass spectra were taken on Gas Chromatograph-Mass Spectrometer LKB 9000. Gas–liquid analyses were performed on Chrom II and Chrom III instruments with flame-ionisation detection. Nitrogen was used as carrier gas and, unless otherwise stated, 20% polypropylene sebacate on Cellite 545 was used as the stationary phase. Preparative gas-liquid chromatography was carried out on a Chrom III instrument.

4-Chloro-3,3,4-trifluoro-2-methyl-1-butanol (*I*)

To a stirred mixture of olefin *VI* (31·8 g, 200 mmol), fused and ground zinc chloride (1 g, 7·4 mmol) and sodium borohydride (2·45 g, 61 mmol) in ether (92 ml) a solution of boron trifluoride etherate (12 g, 80 mmol) in ether (16 ml) was added during 1 hour under nitrogen, the temperature being kept below $25-30°$C. After stirring for 1 hour, the mixture was treated with water (14 ml) and 12% aqueous sodium hydroxide solution (30 ml), and then 30% hydrogen peroxide (30 ml) was added dropwise at $20-30°$C. The ethereal layer was separated, the aqueous one was extracted with ether and the combined ethereal extracts were dried over magnesium sulphate. Evaporation of the solvent followed by rectification afforded 21·2 g (60%) of alcohol *I*, b.p. 78°C/14 Torr. For $C_5H_8ClF_3O$ (176·6) calculated: 34·01% C, 4·57% H, 20·08% Cl, 32·28% F; found: 34·58% C, 4·52% H, 20·02% Cl, 32·37% F. IR spectrum cm^{-1}: $\nu(\text{OH})_{\text{bonded}}$ 3460, $\nu(\text{OH})_{\text{free}}$ 3630. ^{1}H NMR spectrum, δ (p.p.m.): 6·42 (dm, 1 H, $^2J_{\text{HF}} = 48$ Hz, CFClH); 3·75 (d, 2 H, $J = 6$ Hz, C$\underline{\text{H}}_2$); 1·88−2·82 (m, 1 H, C$\underline{\text{H}}$); 2·21 (s, 1 H, OH); 1·13 (d, 3 H, $J = 7$ Hz, C$\underline{\text{H}}_3$).

1-Chloro-1,2,2-trifluoro-4-methyl-3-butanol (*II*) and 4-Chloro-3,3,4-trifluoro-2,2-dimethyl- -1-butanol (*III*)

Trifluorochloroethylene was introduced at a rate 1 l/hour into 2-methyl-1-propanol (100 ml) in a 180 ml quartz ampoule for 23 hours. The ampoule was irradiated with a high-pressure mercury lamp Tesla RVK 250 W, distance 10 cm. The unreacted 2-methyl-1-propanol was distilled off and the residue was fractionated, affording following fractions: 1. fraction boiling at 70 to 85°C/20 Torr (6·5 g), consisting of 74% of *II* and 12% of *III*; 2. fraction b.p. 90—105°C/20 Torr (1·9 g), containing 13% of *II* and 61% of *III*; 3. distillation residue (4·6 g) which was not analysed further and which is probably a mixture of higher telomers. The ratio *II* : *III* (the latter having a longer elution time) was calculated from the composition of the individual fractions to be 72 : 28. Pure alcohols *II* and *III* were obtained by preparative gas–liquid chromatography. For C_6H_{10}. .ClF_3O (190·6) calculated: 37·81% C, 5·28% H, 18·61% Cl, 29·91% F; found: for *II*: 38·28% C, 5·18% H, 18·55% Cl, 29·95% F; for *III*: 37·56% C, 5·10% H, 18·44% Cl, 30·06% F. IR spectrum, cm^{-1}: alcohol *II*: 3455 and 3598; alcohol III: 3415 and 3645 ($\nu(\text{OH})_{\text{bonded}}$ and $\nu(\text{OH})_{\text{free}}$, respectively). ^{1}H-NMR spectrum δ (p.p.m.): alcohol *II*: 6·33 (dt, 0·5 H, $^2J_{\text{HF}} = 47$ Hz, $^3J_{\text{HF}} =$ = 6 Hz, H$\underline{\text{C}}$FCl) and 6·34 (ddd, 0·5 H, $^2J_{\text{HF}} = 47$ Hz, $^3J_{\text{HF}} = 13$ and 6 Hz, H$\underline{\text{C}}$FCl); 4·09 to 3·39 (m, 1 H, CF$_2$C$\underline{\text{H}}$); 2·69 (s, 0·5 H, O$\underline{\text{H}}$) and 2·55 (s, 0·5 H, O$\underline{\text{H}}$); 2·37−1·70 (m, 1 H, C$\underline{\text{H}}$. .(CH$_3$)$_2$); 1·07 (d, 3 H, $J = 6·5$ Hz, C$\underline{\text{H}}_3$) and 1·03 (d, 3 H, $J = 6·5$ Hz, C$\underline{\text{H}}_3$); alcohol *III*: (ddd, 1 H, $^2J_{\text{HF}} = 47·2$ Hz, $^3J_{\text{HF}} = 14·9$ and 1·2 Hz, H$\underline{\text{C}}$FCl); 3·52 (s, 2 H, C$\underline{\text{H}}_2$); 2·64 (s, 1 H, O$\underline{\text{H}}$); 1·10 (s, 6 H, CH$_3$).

5-Chloro-4,4,5-trifluoro-2,3-dimethyl-2-pentanol (*IV*)

A solution of the ester *VIII* (8 g, 39 mmol) in ether (10 ml) was added dropwise to an ethereal solution of methylmagnesium iodide prepared from methyl iodide (11 g, 78 mmol) and magnesium turnings (2·1 g, 83 mmol) in ether (50 ml). The mixture was refluxed for 2 hours and then decomposed with a saturated ammonium chloride solution. The ethereal layer was separated, the aqueous one was extracted three times with ether, the combined ethereal extracts were dried (MgSO$_4$), and taken down. The residue was distilled, affording 5·1 g (64%) of *IV*, b.p. 83°C/17 Torr. For C$_7$H$_{12}$ClF$_3$O (204·6) calculated: 41·09% C, 5·91% H, 27·85% F; found: 41·11% C, 5·85% H, 28·05% F. IR spectrum, cm^{-1}: ν(OH)$_{bonded}$ 3490, ν(OH)$_{free}$ 3602. ^{1}H-NMR spectrum, δ (p.p.m.): 6·67 (dm, 1 H, $^2J_{HF}$ = 48 Hz, $\underline{H}$CFCl); 2·67—1·92 (m, 1 H, C$\underline{H}$); 1·68 (s, 1 H, O$\underline{H}$); 1·25 (bs, 9 H, C$\underline{H}_3$).

4-Chloro-3,3,4-trifluoro-2-methyl-1-butene (*VI*)

Thionyl chloride (129·5 g, 1·08 mol) was added in portions to a mixture of the butanol[9] *V* (147 g, 0·83 mol) and pyridine (73 g, 0·92 mol) under stirring and cooling. The mixture was stirred for 1 hour at room temperature and 3 hours under reflux, and then diluted with water. The organic layer was separated, neutralized with a sodium hydrogen carbonate solution, washed three times with water and dried over magnesium sulphate. Distillation afforded 103 g (71%) of the olefin *VI*, b.p. 92°C, which was identified by comparison of the IR spectra and chromatography with an authentic sample[9].

4-Chloro-3,3,4-trifluoro-2-methylbutanoic Acid (*VII*)

Alcohol *I* (33 g, 0·19 mol) was added at 30°C to a solution of potassium dichromate (117 g, 0·4 mol) in water (700 ml) and conc. sulphuric acid (230 ml). The resulting mixture was heated to 50°C for 15 hours under stirring, then extracted ten times with ether (150 ml) and the combined extracts dried over magnesium sulphate. The solvent was evaporated and the product distilled *in vacuo*, affording the following fractions: 1. fraction, b.p. 39°C/14 Torr (2·9 g), containing mainly acetic acid, as found by IR and ^{1}H-NMR spectra; 2. fraction, b.p. 107°C/14 Torr (26·1 g, 73%) which was shown to be the acid *VII*. For C$_5$H$_6$ClF$_3$O$_2$ (190·6) calculated: 31·52% C, 3·17% H, 18·61% Cl, 29·91% F; found: 32·67% C, 3·48% H, 18·63% Cl, 29·78% F. IR spectrum, cm^{-1}: ν(C=O) 1722, ν(O—H) 3000 cm^{-1}. ^{1}H-NMR spectrum, δ (p.p.m.); 11·90 (s, 1 H, O$\underline{H}$); 6·60 (dm, 1 H, $^2J_{HF}$ = 48 Hz, $\underline{H}$CFCl); 3·83—2·96 (m, 1 H, CF$_2$C$\underline{H}$); 1·52 (d, 3 H, J_{HH} = 7 Hz, C$\underline{H}_3$). The distillation residue (5·6 g) was not investigated.

Methyl 4-Chloro-3,3,4-trifluoro-2-methylbutanoate (*VIII*)

An ethereal diazomethane solution[12] was added to a stirred solution of the acid *VII* (12·8 g, 67 mmol) in ether (20 ml) till the yellow colour persisted. After 10 hours the ether was distilled off and the residue fractionated, affording 8·6 g (63%) of methyl ester *VIII*, b.p. 62°C/16 Torr. For C$_6$H$_8$ClF$_3$O$_2$ (204·6) calculated: 35·23% C, 3·94% H, 17·33% Cl, 27·86% F; found: 36·08% C, 3·92% H, 16·98% Cl, 27·45% F. IR spectrum: ν(C=O) 1748 cm^{-1}. ^{1}H-NMR spectrum, δ (p.p.m.): 6·55 (dm, 1 H, $^2J_{HF}$ = 48 Hz, $\underline{H}$CFCl); 3·75 (s, 3 H, OC$\underline{H}_3$); 3·72—2·83 (m, 1 H, C$\underline{H}$); 1·42 (d, 3 H, J_{HH} = 7 Hz, C$\underline{H}_3$). Mass spectrum, $m/e/$ relative intensity %: 184/4·8 and 186/1·6 (M—HF)$^+$; 173/33 and 175/11 (M—CH$_3$O)$^+$; 137/11 (M—CHClF)$^+$; 125/13; 109/20; 95/11; 91/14; 89/11; 77/12; 67/16 (CFClH)$^+$; 65/13; 59/100 (CO$_2$CH$_3$)$^+$; 51/11; 47/16; 28/15.

Oxidation of *I* with Nitric Acid

Alcohol *I* (20 g, 0·11 mol) was added dropwise to boiling dilute (1 : 1) nitric acid (200 ml). The mixture was boiled under reflux for 15 hours till the oily spots disappeared and then extracted with ether (10 × 40 ml). The combined extracts were dried over magnesium sulphate and the ether was distilled off (water bath). During the distillation of the last remnants of ether, a spotaneous exothermic reaction occurred in the distillation residue, accompanied by evolution of oxides of nitrogen. The residue was distilled *in vacuo* and two fractions were collected: 1. fraction, b.p. 20—120°C/18 Torr (24·3 g), which liberated oxides of nitrogen, and contained water; it was therefore not analysed further; 2. fraction, b.p. 123—4°C/18 Torr (2·6 g, 11%), was identified as 4-chloro-3,3,4-trifluoro-2-hydroxy-2-methylbutanoic acid (*X*) on the basis of comparison of the IR and NMR spectra with the authentic sample.

A solution of this fraction (1·8 g, 8·7 mmol) in ether (10 ml) was treated with diazomethane[12]. The reaction mixture was dried over magnesium sulphate, the solvent evaporated and the residue distilled, affording the ester *XII* (1·7 g, 88%), identical (IR and ^{1}H-NMR spectra) with an authentic sample. According to gas–liquid chromatography, the ester *XII* is accompanied with two compounds of shorter elution time. Both of them were identified on the basis of their mass spectra taken in the course of the gas–liquid chromatography. The second component (5%) was the ester *VIII*, identical with an authentic specimen, the first compound (2%) was found to be methyl 4-chloro-3,3,4-trifluorobutanoate (*XI*). Mass spectrum, m/e relative intensity %: 117/19 and 119/6·4 $(CF_2CFClH)^+$; 82/29 $(C_2HF_3)^+$; 67/23 and 69/8·2 $(CFClH)^+$; 59/100 $(CO_2CH_3)^+$; 31/11.

4-Chloro-3,3,4-trifluoro-2-hydroxy-2-methylbutanoic Acid (*X*)

A mixture of the nitrile *XIV* (2 g, 10·8 mmol) and dilute (1 : 3) sulphuric acid (16 ml) was heated to the boil for 8 hours, then extracted with ether, the extract dried over sodium sulphate, filtered and taken down. Distillation gave 1·77 g (80%) of the acid *X*, b.p. 94—118°C/13 Torr. For $C_5H_6ClF_3O_3$ (206·6) calculated: 29·07% C, 2·92% H, 17·16% Cl, 27·59% F; found: 28·53% C, 3·24% H, 16·93% Cl, 27·48% F. IR spectrum, cm^{-1}: $\nu(C{=}O)$ 1 720 (vs) and 1 760 (s, sh); $\nu(OH)_{bonded}$ 3 050 (ms) and $\nu(OH)_{free}$ 3 520 (ms). ^{1}H-NMR spectrum, δ (p.p.m.): 8·53—7·33 (bs, O$\underline{H}$); 6·55 (ddt, $^2J_{HF}$ = 47 Hz, $^3J_{HF}$ = 13 and 2 Hz, C$\underline{H}$ClF); 1·69 (s, C$\underline{H}_3$).

Methyl 4-Chloro-3,3,4-trifluoro-2-hydroxy-2-methylbutanoate (*XII*)

An ethereal solution of diazomethane, prepared from N-nitrosomethylurea (1 g, 9·6 mmol) and 70% potassium hydroxide solution (2 ml), was added dropwise to a solution of the hydroxy acid *X* (1·77 g; 8 mmol) in ether (10 ml). Evaporation of the solvent and distillation afforded 1·54 g (87·5%) of the ester *XII*, b.p. 71—89°C/30 Torr. For $C_6H_8ClF_3O_3$ (220·6) calculated: 32·66% C, 3·65% H, 16·07% Cl, 25·84% F; found: 33·18% C, 3·81% H, 16·30%Cl, 24·96% F. IR spectrum, cm^{-1}: $\nu(C{=}O)$ 1 743 (vs) and $\nu(OH)_{bonded}$ 3 490 (ms). ^{1}H-NMR spectrum, δ (p.p.m.): 6·52 (ddm, $^2J_{HF}$ = 47·0 Hz, $^3J_{HF}$ = 11·0 Hz, $\underline{H}$CFCl); 3·96 (s, O$\underline{H}$); 3·90 and 3·87 (s, C$\underline{H}_3$O); 1·60 and 1·57 (s, C$\underline{H}_3$O).

4-Chloro-3,3,4-trifluoro-2-hydroxy-2-methylbutanenitrile (*XIV*)

A saturated aqueous potassium cyanide solution (2 g; 0·04 mol) was added dropwise under cooling with ice to a stirred emulsion of the ketone[11] *XIII* (3·20 g; 0·02 mol) in water (3 ml) and conc. sulphuric acid (1·4 g; 0·014 mol). An orange-yellow oil was formed during the reaction. The mixture was set aside for 6 hours with intermittent stirring, the organic layer was separated,

the aqueous solution extracted with ether and the ethereal extract dried over sodium sulphate. Before distilling off the ether, the ethereal extract was acidified with conc. sulphuric acid; the residue after the evaporation of solvent was combined with the separated aqueous layer and, upon further acidification with sulphuric acid, the product was distilled *in vacuo*. The resulting cyanohydrin *XIV* (2·9 g, 75%) boiled at 93°C/12 Torr. Pure *XIV* is unstable in alkaline medium and decomposes at elevated temperature into the starting components. When acidified with conc. sulphuric acid, it can be stored or distilled. For $C_5H_5ClF_3NO$ (187·6) calculated: 32·02% C, 2·69% H, 30·39% F, 18·90% Cl, 7·47% N; found: 31·48% C, 2·88% H, 30·17% F, 18·81% Cl, 7·93% N. IR spectrum, cm^{-1}: $\nu(CN)$ 1705 (w), $\nu(OH)_{bonded}$ 3380 (ms), and $\nu(OH)_{free}$ 3590 (w). ^{1}H-NMR spectrum, δ (p.p.m.): 6·50 (ddt, $^2J_{HF} = 48$ Hz, $^3J_{HF} = 13$ and 3 Hz, C$\underline{H}$ClF); 4·03 (s, OH); 1·82 (bs, C$\underline{H}_3$).

4-Chloro-3,3,4-trifluoro-2-methyl-1,2-butanediol (*XV*)

A) A 5% aqueous solution of potassium permanganate (700 ml) was added dropwise under stirring to the butene *VI* (50 g, 0·26 mol) at 0°C. The mixture was stirred for 2 hours, acidified with hydrochloric acid, and manganese dioxide was reduced with sodium sulphite. The solution was extracted with ether, the extract dried over magnesium sulphate, the solvent evaporated and the product distilled, yielding 26 g (47%) of the diol *XV*, b.p. 112°C/20 Torr. Two diastereoisomeric racemates *XVa* and *XVb* were detected by analytical, and separated by preparative, gas–liquid chromatography (15% Reoplex on Chromaton N-AW). For $C_5H_8ClF_3O_2$ (192·6) calculated: 31·18% C, 4·19% H, 18·41% Cl, 29·61% F; found for *XVa*: 30·98% C, 3·85% H, 18·54% Cl, 29·42% F; found for *XVb*: 31·05% C, 3·71% H, 18·31% Cl, 29·42% F. The IR spectra of both epimers were identical: $\nu(OH)_{bonded}$ 3500 cm^{-1}, $\nu(OH)_{free}$ 3600 cm^{-1}. ^{1}H-NMR spectrum, δ (p.p.m.): for *XVa*: 6·58 (ddm, $^2J_{HF} = 46$ Hz, $^3J_{HF} = 16$ Hz, C$\underline{H}$ClF); 4·05—3·43 (q, C$\underline{H}_2$); 3·28 (s, OH); 1·30 (bs, C$\underline{H}_3$); for *XVb*: 6·53 (ddm, $^2J_{HF} = 47$ Hz, $^3J_{HF} = 13$ Hz, C$\underline{H}$ClF); 3·98 to 3·44 (q, C$\underline{H}_2$); 2·68 (s, O$\underline{H}$); 1·38 (bs, C$\underline{H}_3$).

B) A slurry of lithium aluminium hydride (0·2 g, 5·3 mmol) in ether (20 ml) was added dropwise to a solution of the ester *XII* (1·1 g, 5 mmol) in ether (10 ml). The mixture was decomposed with water (2 ml) and dilute (1 : 1) hydrochloric acid (20 ml). The ethereal layer was separated, the aqueous layer was extracted three times with ether, the combined ethereal extracts were washed with an aqueous sodium hydrogen carbonate solution and dried over magnesium sulphate. The solvent was evaporated and the residue distilled at 109°C/19 Torr, affording 1 g of the diol *XV*. Comparison (gas–liquid chromatography, IR and NMR spectra) with the sample prepared under *A)* has shown that the product is a mixture of diastereoisomeric racemates *XVa* and *XVb*.

Reaction of the Olefin *VI* with Tert-butyl Hypochlorite

A) A solution of tert-butylhypochlorite (14 g; 0·13 mol) in acetone (28 ml) was added to a stirred solution of the olefin *VI* (19 g; 0·12 mol) in water (60 ml) and acetone (40 ml). The mixture was stirred for 15 hours at room temperature, and diluted with ether. The organic layer was separated, the aqueous one extracted three times with ether and the combined ethereal extracts dried over magnesium sulphate. The solvents and the tert-butyl alcohol were distilled off and the residue (12·4 g) was fractionated. The fractions boiling at 30—83°C/18 Torr were chromatographically non-homogeneous. The principal product of the reaction, 2,4-dichloro-3,3,4-trifluoro-2-methylbutanol (*XVI*), was accompanied by compounds of shorter elution time: 1,2,4-trichloro-3,3,4-trifluoro-2-methylbutane (*XVIII*), 4-chloro-2-chloromethyl-3,3,4-trifluoro-1-butene (*XIX*), chloroacetone, and further two unidentified compounds. According to gas–liquid chromatography, the product composition is *XVI* : *XVIII* : *XIX* = 67 : 12 : 8. Compounds *XVI*,

XVIII, XIX and chloroacetone were isolated by preparative gas–liquid chromatography. Chromatography of the alcohol *XVI* has shown it to be a mixture of diastereoisomeric racemates.

Alcohol XVI: IR spectrum, cm^{-1}: $v(OH)_{bonded}$ 3410 (ms) and $v(OH)_{free}$ 3600 and 3632 (ms). ^{1}H-NMR spectrum, δ (p.p.m.): 6·70 (dd, $^2J_{HF} = 47$ Hz, $^3J_{HF} = 15$ Hz, HCFCl); 3·90 (s, CH_2); 2·90 (s, OH); 1·75 (s, CH_3). Mass spectrum, $m/e/$ relative intensity %: 160/48, 162/33, and 164/5·6 (M—CF_2)$^+$; 93/12; 91/11; 89/12; 67/15 (CFClH)$^+$; 57/14; 51/11; 39/14; 31/100 (CH$_2$OH)$^+$; 29/30; 28/11.

Compound XVIII: ^{1}H-NMR spectrum, δ (p.p.m.): 6·72 (dd, $^2J_{HF} = 47$ Hz, $^3J_{HF} = 15$ Hz, CHFCl); 3·90 (s, CH_2); 1·85 (s, CH_3). Mass spectrum, $m/e/$ relative intensity %: 111/100, 113/66 and 115/12 (M-117)$^+$; 91/12; 77/16; 75/36; 67/27 and 69/10 (CFClH)$^+$; 65/25; 51/13; 49/15 (CH$_2$Cl)$^+$; 39/23; 28/34.

Olefin XIX: IR spectrum: $v(=CH_2)$ 1750 cm^{-1} (ms). ^{1}H-NMR spectrum, δ (p.p.m.): 6·29 (ddd, $^2J_{HF} = 49$ Hz, $^3J_{HF} = 5·5$ and 7 Hz, CHClF); 5·88 (bs, $=CH_2$); 4·20 (bs, CH_2Cl). Mass spectrum, $m/e/$ relative intensity %: 192/3 (M)$^+$; 160/12; 127/28; 125/84 (M-67)$^+$; 109/12; 89/28; 77/11; 67/17 (CFClH)$^+$; 51/14; 39/20; 32/28; 29/15; 28/100.

B) To a stirred solution of the olefin *VI* (68·2 g, 0·43 mol) in water (460 ml) and acid (60 ml) was added tert-butyl hypochlorite (46 g, 0·42 mol) during 30 minutes and the resulting mixture was stirred for 5 hours. The lower oily layer was separated and the aqueous layer was extracted with ether. The ethereal extract was combined with the separated layer, dried over magnesium sulphate and taken down. Rectification of the residue afforded 51·9 g of a fraction, b.p. 98 to 104°C/21 Torr, containing 2,4-dichloro-3,3,4-trifluoro-2-methyl-1-butyl acetate *(XVII)* and the alcohol *XVI* in the ratio 87 : 13. Further rectification of this product gave the pure acetate *XVII*, b.p. 107°C/24 Torr. For $C_7H_9Cl_2F_3O_2$ (253·1) calculated: 33·22% C, 3·59% H, 28·02% Cl, 22·52% F; found: 33·45% C, 3·55% H, 28·81% Cl, 21·64% F. IR spectrum: $v(C=O)$ 1756 cm^{-1} (vs). ^{1}H-NMR spectrum, δ (p.p.m.): 6·66 (ddd, $^2J_{HF} = 48$ Hz, $^3J_{HF} = 12$ and 3 Hz, CHClF); 4·46 and 4·37 (s, CH_2); 2·14 (s, $COCH_3$); 1·77 (bs, CH_3).

C) A mixture of the olefin *VI* (158·6 g; 1 mol), glacial acetic acid (198 ml = 180·3 g; 3 mol) and tert-butyl hypochlorite (108·6 g; 1 mol) was stirred for 7 hours at room temperature. Fractions boiling under 140°C were distilled off and the residue was fractionated, affording 178 g (70%) of the acetate *XVII*, b.p. 96—101°C/16 Torr, which was identical with the sample obtained in the experiment *B*. Gas–liquid chromatography proved the presence of trichloro derivative *XVIII* and of the olefin *XIX* in the lower boiling fractions.

2,4-Dichloro-3,3,4-trifluoro-2-methylbutanoic Acid *(XX)*

The acetate *XVII* (17·8 g), containing 33% of the alcohol *XVI*, was added to a solution of potassium dichromate (44·2 g; 0·15 mol) in water (375 ml) and conc. sulphuric acid (75 ml). The mixture was stirred at 70°C for 5 hours, and then extracted ten times with ether. The combined ethereal extracts were dried over magnesium sulphate, taken down and the residue fractionated, giving 5·4 g of the acid *XX*, b.p. 117—120°C/20 Torr. IR spectrum, cm^{-1}: $v(C=O)$ 1730 (w), $v(OH)_{bonded}$ 3050 (ms), $v(OH)_{free}$ 3500 (vw). ^{1}H-NMR spectrum, δ (p.p.m.): 11·1 (bs, OH); 6·73 (ddm, $^2J_{HF} = 48$ Hz, $^3J_{HF} = 14$ Hz, CHClF); 1·95 (s, CH_3).

Methyl 2,4-Dichloro-3,3,4-trifluoro-2-methylbutanoate *(XXI)*

A solution of the acid *XX* (5 g) in ether (15 ml) was treated with an ethereal solution of diazomethane in the usual manner. The methyl ester *XXI* (3·0 g) was isolated by distillation, b.p.

81 — 82°C/20 Torr. For $C_6H_7Cl_2F_3O_2$ (239·0) calculated: 30·15% C, 2·95% H, 29·67% Cl, 23·84% F; found: 30·80% C, 2·96% H, 30·76% Cl, 23·98% F. IR spectrum, cm^{-1}: ν(C=O) 1747 (vs) and 1763 (vs). ^{1}H-NMR spectrum, δ (p.p.m.): 6·72 (ddm, $^2J_{HF} = 47$ Hz, $^3J_{HF} = 14$ Hz, C$\underline{H}$ClF); 3·83 (s, C$\underline{H}_3$O); 1·92 (bs, C$\underline{H}_3$).

3,3,4-Trifluoro-2-isopropyloxetane (*XXII*) and 2,3,3-Trifluoro-4,4-dimethyloxolane (*XXIII*)

A fraction (5·8 g), containing 54% of butanol *III*, 27% of pentanol *II* and 19% of unidentified compounds was refluxed for 7 hours under stirring with a solution of potassium hydroxide (6·1 g) in water (23 ml). The reaction mixture afforded 3·4 g of a product which was dried over magnesium sulphate. According to gas–liquid chromatography, the product contained 2 compounds which were separated by preparative gas–liquid chromatography. The compound with shorter elution time (36% of the mixture) was shown to be the oxetane *XXII*, the other compound the oxolane *XXIII*. For $C_6H_9F_3O$ (154·1) calculated: 46·75% C, 5·89% H, 36·98% F; found for *XXII*: 47·04% C, 5·78% H, 36·78% F, found for *XXIII*: 47·50% C, 5·87% H, 38·80% F. ^{1}H-NMR spectrum, δ (p.p.m.): oxetane *XXII*: 5·81 (dm, $^2J_{HF} = 68$ Hz, C$\underline{H}$F); 4·81—4·02 (m, C$\underline{H}$CF$_2$); 2·36—1·72 (m, C$\underline{H}$—CH$_3$); 0·95 (d, $J_{HH} = 7·3$; C$\underline{H}_3$) and 1·00 (d, $J_{HH} = 7·3$, CH$_3$); oxolane *XXIII*: 5·43 (ddd, $^2J_{HF} = 65$ Hz, $^3J_{HF} = 5$ and 1·2 Hz, C$\underline{H}$F); 4·07—3·75 (m, 2 H, C$\underline{H}_2$); 1·24 (d, C$\underline{H}_3$); and 1·17 (d, C$\underline{H}_3$). Mass spectrum of *XXIII*, $m/e/$ relative intensity %: 154/0·1 (M)$^+$; 153/0·5 (M—1)$^+$; 139/0·7 (M—15)$^+$; 109/15 $(C_4H_4F_3)^+$; 106/23 (M—CHFO)$^+$; 91/100 $(C_4H_5F_2)^+$, 65/20; 43/11; 41/15; 39/15; 29/12; 27/10.

2,3,3-Trifluoro-4-methyloxolane (*XXIV*)

A stirred mixture of alcohol *I* (4 g, 23 mmol) and a solution of sodium hydroxide (4·6 g, 110 mmol) in water (17 ml) was refluxed for 6 hours. From the mixture an oily product was distilled which, upon drying over magnesium sulphate, afforded the chromatographically pure oxolane *XXIV* (1·7 g), b.p. 96—98°C. According to gas–liquid chromatography (50 m capillary column, dinonyl phthalate), the product was a 57 : 43 mixture of both diastereoisomers of *XXIV*; they were analysed together and their structure was proved by mass spectrometry. For $C_5H_7F_3O$ (140·1) calculated: 42·84% C, 5·04% H, 40·69% F; found: 43·28% C, 5·19% H, 40·75% F. ^{1}H-NMR spectrum, δ (p.p.m.): 5·38 (d, 0·5 H, $^2J_{HF} = 65$ Hz, $\underline{H}$CF) and 5·45 (ddd, 0·5 H, $^2J_{HF} = 63$ Hz, $^3J_{HF} = 4$ and 1·8 Hz, $\underline{H}$CF); 4·34 (td, 1 H, $^3J_{HF} = 9$ and 2 Hz, CH$_2$) and 3·97—3·29 (m, 1 H, CH$_2$); 3·06—2·17 (m, 1 H, CH); 1·19 (d, 1·5 H, $J_{HH} = 7$ Hz, CH$_3$) and 1·16 (d, 1·5 H, $J_{HH} = 7$ Hz, CH$_3$). Mass spectrum, $m/e/$ relative intensity %: 139/0·4 (M—1)$^+$; 125/0·4 (M—15)$^+$; 121/1·3 (M—19)$^+$; 95/10 $(C_3H_2F_3)^+$; 92/38 (M—CHFO)$^+$; 77/100 $(C_3H_3F_2)^+$; 51/14; 41/14; 39/10; 29/11; metastable ion for: $92^+ \rightarrow 77^+ + 15$.

4,4,5-Trifluoro-2,2,3-trimethyloxolane (*XXV*)

A mixture of alcohol *IV* (5·2 g; 25 mmol) and sodium hydroxide (5·1 g) in water (19 ml) was refluxed for 4 hours. Subsequent steam-distillation yielded 2·8 g (65%) of a crude product which was dried and distilled to afford 2·1 g of oxolane *XXV*; b.p. 113°C. Gas–liquid chromatography revealed the presence of two diastereoisomers (62 : 38) which were separated by means of preparative gas–liquid chromatography (polypropylene sebacate, 360 cm, 80°C, hydrogen as carrier gas). For $C_7H_{11}F_3O$ (168·2) calculated: 50·00% C, 6·59% H, 33·89% F; found: 51·53% C, 5·10% H, 33·99% F. ^{1}H-NMR spectrum, δ(p.p.m.): for *XXVa*: 5·44 (d, 1 H, $^2J_{HF} = 65$ Hz,

C$\underline{H}$F); 2·87—1·83 (m, 1 H, C$\underline{H}$); 1·35 and 1·11 (s, 6 H, C(C$\underline{H}_3$)$_2$); 1·02 (d, 3 H, CHC$\underline{H}_3$); for *XXVb*: 5·60 (dd, 1 H, $^2J_{HF} = 65$ Hz, $^3J_{HF} = 6$ Hz, C$\underline{H}$F); 2·70—1·66 (m, 1 H, C$\underline{H}$); 1·33 and 1·24 (s, 6 H, C(C$\underline{H}_3$)$_2$); 1·05 (dd, 3 H, $J_{HH} = 7·5$ Hz and $J = 2$ Hz, CHC$\underline{H}_3$). Mass spectra of both isomers were identical; m/e/ relative intensity%: 168/0·3 (M)$^+$; 153/100 (M—15)$^+$; 105/67 (C$_5$H$_7$F$_2$)$^+$; 95/19 (C$_3$H$_2$F$_3$)$^+$; 77/18; 61/16; 59/48; 56/12; 55/12; 43/68; 42/22; 41/36; 39/24; 29/10; 28/14; 27/16.

Cyclisation of Acetate *XVII*

A) A mixture of the acetate *XVII* (15·3 g; 0·06 mol) and a potassium hydroxide solution (10 g, 0·18 mol, in 27 ml of water) was stirred at room temperature for 2 days. The mixture was steam-distilled, and the crude product (9 g) dried over magnesium sulphate, affording 6·8 g (65%) of a product, b.p. 133·5—135°C, which contained (according to gas–liquid chromatography) four components. The first two compounds were shown by mass spectrometry to be the diastereoisomers of 4-chloro-4-methyl-2,3,3-trifluorooxolane (*XXVI*) and they were identical (gas–liquid chromatography and mass spectrometry) with the samples of *XXVI*, prepared according to the procedure *B*. The second two compounds with longer elution times were identified as the diastereoisomeric 2-methyl-2-(2-chloro-1,1,2-trifluoroethyl)oxirane (*XXVII*). The ratio *XXVI* : *XXVII* was 15 : 85. For C$_5$H$_6$ClF$_3$O (174·6) calculated: 34·41% C, 3·46% H, 20·31% Cl, 32·66% F; found: 34·50% C, 3·50% H, 20·52% Cl, 31·73% F. The mixture was enriched in the oxirane *XXVII* (95% purity) by fractionation. ^{1}H-NMR spectrum, δ (p.p.m.): 6·20 (dm, 1 H, $^2J_{HF} = 48$ Hz, CFCl$\underline{H}$); 3·12 and 2·71 (d, 1 H and m, 1 H, C$\underline{H}_2$); 1·56 (s, 3 H, C$\underline{H}_3$). Mass spectrum, m/e/ relative intensity %: 159/6 (M—15)$^+$; 139/56 (M—Cl)$^+$; 109/11; 107/36 (M—CHFCl)$^+$; 91/14; 89/17; 81/11; 77/42; 75/11; 69/14; 67/28 (CFClH)$^+$; 59/31; 57/89 (M—HCFClCF$_2$)$^+$; 51/69; 43/100; 42/11; 41/11; 39/39; 33/14; 29/89; 28/17; 27/56.

B) A mixture of an aqueous potassium hydroxide solution (112·2 g; 2 mol in 300 ml) and acetate *XVII* (126·6 g; 0·5 mol) was stirred for 8 hours at 80°C and then steam-distilled. The lower layer of the distillate was separated, dried over magnesium sulphate and fractionated (23·8 g), affording 8 g of a fraction, boiling at 121—135°C, which was identified as a mixture of diastereoisomeric racemates of oxolane *XXVI*. Their mass spectra were identical: m/e/ relative intensity %: 139/7 (M—Cl)$^+$; 109/21 (M—Cl—CH$_2$O)$^+$; 91/100 (M—Cl-CHFO)$^+$; 89/10; 65/20; 64/10; 59/10; 57/11; 51/18; 41/14; 39/27; 31/10; 29/23; 28/10. ^{1}H-NMR spectrum, δ (p.p.m.): 5·69 (dd, $^2J_{HF} = 64$ Hz and $^3J_{HF} = 5$ Hz, 1/3 CHF) and 5·61 (dd, $^2J_{HF} = 64$ Hz, $^3J_{HF} = 5$ Hz, 2/3 CHF); 4·52—4·02 (m, C$\underline{H}_2$); 1·76 to 1·69 (m, C$\underline{H}_3$).

4-Chloro-3,3,4-trifluoro-1,2-butanediol (*XXVIII*)

A 5% aqueous solution (250 ml) of potassium permanganate was added to butene *XXIX* (17 g; 94·5 mmol) under stirring and cooling. The work-up procedure was the same as described for the hydroxylation of the olefin *VI*. Distillation afforded 9·5 g (45%) of the diol *XXVIII*, b.p. 124°C/30 Torr. For C$_4$H$_6$ClF$_3$O$_2$ (178·6) calculated: 26·91% C, 3·40% H, 19·85% Cl, 31·92% F; found: 26·48% C, 3·12% H, 19·92% Cl, 31·94% F. IR spectrum, cm^{-1}: ν(OH)$_{bonded}$ 3400, ν(OH)$_{free}$ 3600. ^{1}H-NMR spectrum, δ (p.p.m.): 6·74—6·05 (dm, 1 H, $^2J_{HF} = 48$ Hz, $\underline{H}$CFCl); 4·38—4·00 (m, 1 H, C$\underline{H}$); 4·00—3·85 (m, 2 H, C$\underline{H}_2$); 3·85 (s, 2 H, OH).

4-Chloro-3,3,4-trifluoro-1-butene (*XXIX*)

Acetate *XXX* was pyrolyzed at 550°C in a flask, filled up to 1/3 with Berle saddles. The acetate *XXX* was added at such a rate, as to maintain the head temperature at 80—110°C. The crude

product was neutralized with a 10% sodium hydroxide solution, washed twice with water and dried over magnesium sulphate. Fractionation afforded olefin *XXIX*, b.p. 68°C. The pyrolysis proceeds with 40% conversion; the yield of the olefin, based on the reacted acetate, is 76%. For $C_4H_4ClF_3$ (144·5) calculated: 33·24% C, 2·79% H, 24·52% Cl, 39·45% F; found: 33·09% C, 2·96% H, 24·18% Cl, 39·23% F. IR spectrum: $\nu(C=C)$ 1750 cm^{-1} (m). Mass spectrum, m/e relative intensity %; 67/7; 69/3 $(CFClH)^+$; 77/100 $(CH_2=CHCF_2)^+$; 89/10 $(M-Cl-HF)^+$; 109/2 $(M-Cl)^+$; 144/0·5 $(M)^+$.

4-Chloro-3,3,4-trifluoro-2-butyl Acetate (*XXX*)

A mixture of butanol *XXXI* (110 g; 0·68 mol), acetic anhydride (120 g, 1·18 mol) and sulphuric acid (5 drops) was heated to 160—170°C for 1 hour, cooled, and diluted with water. The ester layer was neutralized with a sodium carbonate solution, washed with water, dried over magnesium sulphate and taken down. Distillation of the residue gave 132 g (96%) of the acetate *XXX*, b.p. 81°C/45 Torr. For $C_6H_8ClF_3O_2$ (204·6) calculated: 35·22% C, 3·95% H, 27·86% F, 17·33% Cl; found: 35·27% C, 4·08% H, 28·00% F, 17·82% Cl. Mass spectrum, m/e relative intensity%: 149/2·4 $(CF=CH(OAc)-CH_3)^+$; 136/0·6 $(CH_3CH(OAc)CF_2)^+$; 87/10 $(CH_3CHOAc)^+$; 43/100 $(CH_3CO)^+$; 15/5 $(CH_3)^+$.

1,3-Dichloro-1,2,2-trifluorobutane (*XXXII*)

Thionyl chloride (13 g; 0·11 mol) was added dropwise to a stirred and cooled solution of the butanol *XXXI* (10 g; 0·082 mol) in pyridine (7·2 g; 0·092 mol). The mixture was heated for 5 hours to the boil, diluted with water, the organic layer neutralized with a sodium hydrogen carbonate solution, washed with water, dried over magnesium sulphate and taken down. Distillation afforded 6·6 g (58%) of *XXXII*, b.p. 104—105°C. For $C_4H_5Cl_2F_3$ (181·0) calculated: 26·54% C, 2·79% H, 39·17% Cl, 31·49% F; found: 27·01% C, 2·85% H, 38·93% Cl, 31·48% F. ^{1}H-NMR spectrum, δ (p.p.m.): 6·86—6·08 (dm, 1 H, $^2J_{HF} = 50$ Hz, $\underline{H}$CFCl); 4·58—4·14 (m, 1 H, C$\underline{H}$CH$_3$); 1·66 (d, 3 H, $J_{HH} = 6$ Hz, C$\underline{H}_3$CH). Mass spectrum, m/e / relative intensity %: 182/0·4; 180/1·0 $(M)^+$; 162/1·6; 160/4; 146/1·5; 144/6; 115/11; 113/32; 69/16; 67/35; 65/41; 63/100.

2,3,3-Trifluoro-4-hydroxy-4-methyloxolane (*XXXIII*)

A solution of diol *XV* (10 g; 0·052 mol) in 25% ethanolic potassium hydroxide solution (25 ml) was refluxed for 2 hours. The separated potassium chloride was filtered off, the filtrate taken down and the residue distilled, affording 6·9 g (84·5%) of the oxolane *XXXIII*, b.p. 57°C/18 Torr. For $C_5H_7F_3O_2$ (156·1) calculated: 38·46% C, 4·53% H, 36·51% F; found: 38·11% C, 4·38% H, 36·48% F. According to gas–liquid chromatography, the product is a mixture (54 : 46) of two diastereoisomers which were isolated in the pure state by preparative gas–liquid chromatography (15% Reoplex on Chromaton N-AW, 140°C, hydrogen as carrier gas). IR spectra were identical for both isomers: $\nu(OH)_{bonded}$ 3420 cm^{-1}, $\nu(OH_{free})$ 3600 cm^{-1}. ^{1}H-NMR spectrum, δ (p.p.m.) isomer *XXXIIIa*: (5·62 (ddd, 1 H, $^2J_{HF} = 64$ Hz, $^3J_{HF} = 6$ Hz, C$\underline{H}$F); 4·36—3·82 (m, 2 H, C$\underline{H}_2$); 2·90 (s, 1 H, OH); 1·42 (d, 3 H, C$\underline{H}_3$); isomer *XXXIIIb*: 5·68 (dd, 1 H, $^2J_{HF} = 64$ Hz, $^3J_{HF} = 2$ Hz, C$\underline{H}$F); 4·24—3·94 (m, 2 H, C$\underline{H}_2$); 2·78 (s, 1 H, O$\underline{H}$); 1·45 (d, 3 H, C$\underline{H}_3$). Mass spectra of both isomers were identical; m/e / relative intensity %: 156 3 $(M)^+$; 136/5; 111/7; 107/6; 93/6; 91/15; 73/11; 58/8; 57/13; 45/13; 44/6; 43/100; 42/26; 41/14; 31/12; 29/18; 27/8; 15/8.

4,4,5-Trifluoro-3-hydroxyoxolane (*XXXIV*)

A solution of the diol *XXVIII* (5 g; 0·028 mol) in 25% ethanolic potassium hydroxide solution (16 ml) was treated as described for the preparation of the oxolane *XXXIII*. Distillation afforded 3·2 g (80·5%) of the oxolane *XXXIV*, b.p. 54°C/30 Torr. For $C_4H_5F_3O_2$ (142·1) calculated: 33·81% C, 3·55% H, 40·12% F; found: 33·46% C, 3·77% H, 39·58% F. Gas–liquid chromatographic analysis revealed two diastereoisomeric racemates (45 : 55) which were isolated by preparative gas–liquid chromatography. ^{1}H-NMR spectrum, δ (p.p.m.): isomer *XXXIVa*: 5·60 (dm, 1 H, $^2J_{HF} = 65$ Hz, CHF); 4·56 — 4·10 (m, 3 H, CH_2 and CH); 2·60 (s, 1 H, OH); isomer *XXXIVb*: 5·60 (dd, 1 H, $^2J_{HF} = 62$ Hz, CFH); 4·60 — 4·30 (m, 2 H, CH_2); 4·02 — 3·82 (m, 1 H CH); 2·24 (s, 1 H, OH). Mass spectra of both isomers were identical; m/e / relative intensity %: 142/0·3 $(M)^+$; 122/6; 111/5; 94/41; 92/24; 74/42; 64/25; 62/29; 46/53; 43/50; 42/82; 31/92; 30/11; 29/100; 27/19; 15/18.

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