CLEAVAGE OF 3,3,4-TRIFLUORO-2,2-DIMETHYLOXETANE BY MINERAL ACIDS*

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Cleavage of 3,3,4-trifluoro-2,2-dimethyloxetane (*I*) in an aqueous solution of sulphuric acid, phosphoric acid, hydrogen chloride, or hydrogen bromide gave a mixture of 2,2-difluoro-3-methyl--3-butenal (*II*) and 5,5-difluoro-2-(1,1-difluoro-2-hydroxy-2-methylpropyl)-4-hydroxy-6,6-dimethyl-1,3-dioxane (*VIa*); in the cleavage effected by hydrochloric or hydrobromic acid the mixture also contained 3-chloro- or 3-bromo-2,2-difluoro-3-methyl-1,1-butanediol (*Vb* or *Vc*). In alcoholic solutions of the mineral acids the cleavage afforded the corresponding acetals of butenal *II* and 2,2-difluoro-3-hydroxy-3-methylbutanal (*IIIa*). The action of sulphuric acid in the presence of acetyl chloride or acetanhydride led to 1-chloro-2,2-difluoro-3-methyl-3-butenyl acetate (*IVd*) or 2,2-difluoro-3-methyl-3-butenylidene diacetate (*IVe*), as the main product. Butenal *II* was a sole product of the cleavage of oxetane *I* by polyphosphoric acid at 150—160°C in the gaseous phase. At temperatures above 180°C there were also formed (in addition to butenal *II*) 1,1,5,5-tetrafluoro-2,6-dimethyl-1,6-heptadiene-4-ol (*IX*) and its formate (*X*).

The cleavage of 3-fluorooxetane by mineral acids, first described by Boguslavskaya[1,2], gives the expected fluoro diols and their derivatives. However, oxetanes fluorinated to higher degrees are extraordinarily resistant to the acidolysis[3]. In the case of 3,3,4--trifluoro-2,2-dimethyloxetane (*I*), the preparation of which we had described earlier[4], the oxetane ring would not open readily enough until concentrated mineral acids were used, in aqueous or non-aqueous media, when the cleavage was accompanied by liberation of hydrogen fluoride. The typical reaction products were 2,2-difluoro--3-methyl-3-butenal (*II*), which is the sole product of the cleavage of oxetane *I* by polyphosphoric acid, and 2,2-difluoro-3-hydroxy-3-methylbutanal (*IIIa*) or its cyclic dimer *VIa*; the latter was formed in all systems containing water and was the main product of the cleavage effected with 80% sulphuric acid. The formation of the two types of product corresponds to two possible conversions of the postulated carbocation *Ib*, *i.e.* elimination of a proton and a molecule of hydrogen fluoride, leading to the unsaturated aldehyde *II*, or a nucleophilic attack in which hydrogen fluoride is released and an aldehyde of the common formula *III* is formed (Scheme 1).

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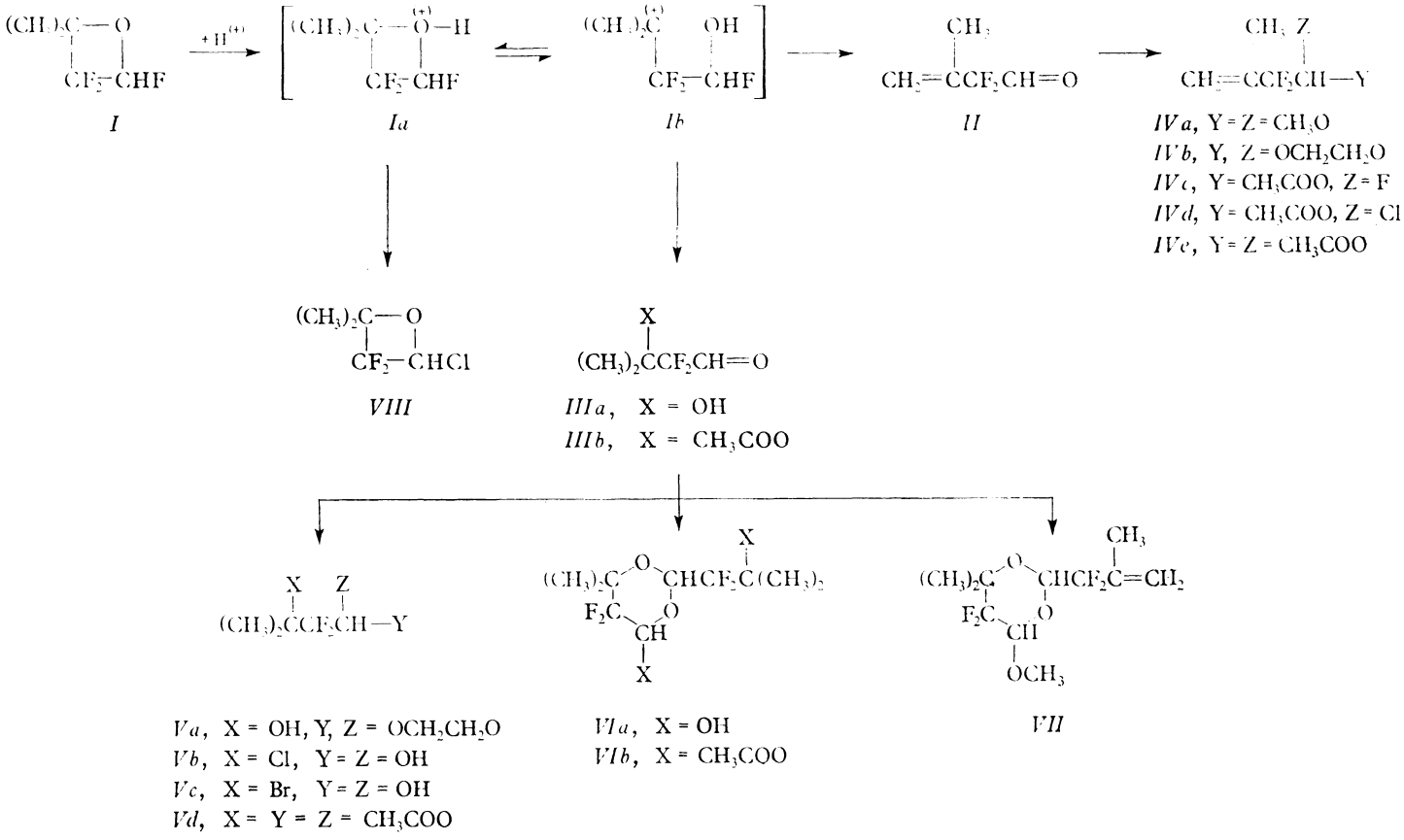

I
Ia
Ib
II
IVa, Y = Z = CH3O
IVb, Y, Z = OCH2CH2O
IVc, Y = CH3COO, Z = F
IVd, Y = CH3COO, Z = Cl
IVe, Y = Z = CH3COO
VIII
IIIa, X = OH
IIIb, X = CH3COO
Va, X = OH, Y, Z = OCH2CH2O
Vb, X = Cl, Y = Z = OH
Vc, X = Br, Y = Z = OH
Vd, X = Y = Z = CH3COO
VIa, X = OH
VIb, X = CH3COO
VII

SCHEME 1

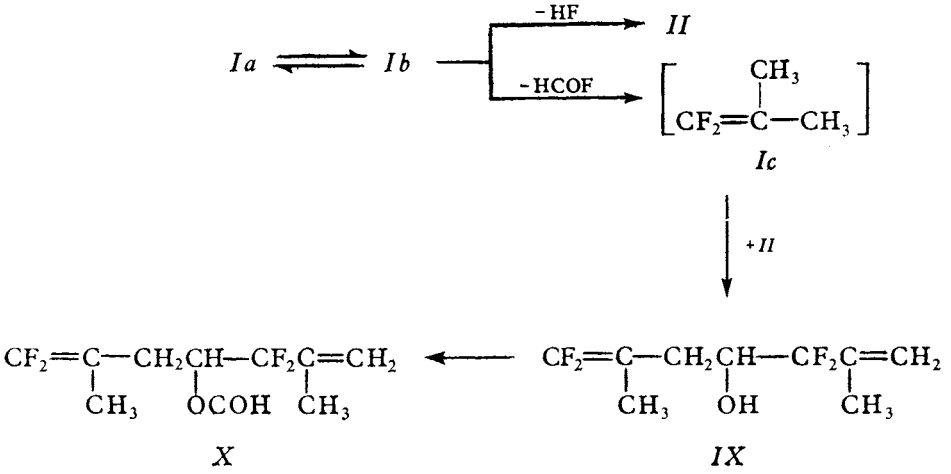
Most of the products that we isolated and identified can be accounted for as due to subsequent reactions of the aldehydes *II* and *III* in the reaction medium. In the cleavage by 35% hydrochloric acid and/or 47% hydrobromic acid there were also formed considerable amounts of the aldehyde hydrates *Vb* and *Vc*, respectively, and the chlorinated oxetane *VIII*; the analogous bromo derivative was not detected. The substitution at the 4-position probably occurs in the protonized form of oxetane *Ia*, since direct displacement of the fluorine atom by an exposed chloride anion does not occur in such systems[3,5]. The action of 85% phosphoric acid did not produce any cleavage until the temperature was elevated; in the use of 40% perchloric acid at 60°C no visible reaction occurred even in the course of hours.

We also attempted cleavage of the oxetane *I* by solutions of sulphuric and/or hydrochloric acids in methanol, ethylene glycol, acetyl chloride or acetanhydride. In the methanolic solution of sulphuric acid the reaction occurred only after elevating the temperature and led to a complex mixture, from which we isolated the main constituent only, *viz.* 5,5-difluoro-2-(1,1-difluoro-2-methyl-2-propenyl)-4-methoxy--6,6-dimethyl-1,3-dioxan (*VII*). Several days' standing of the oxetane *I* in methanol pre-saturated with hydrogen chloride produced a slow cleavage to butenal *II*, butanediol *Vb*, and a greater quantity of 2,2-difluoro-3-methyl-3-butenaldimethyl acetal (*IVa*). A ready and clear-cut cleavage was effected with a solution of sulphuric acid in ethylene glycol, affording a mixture of 2-(1,1-difluoro-2-methyl-2-propenyl)-1,3-dioxolane (*IVb*) and 2-(1,1-difluoro-2-hydroxy-2-methylpropyl)-1,3-dioxolane (*Va*). The dioxolanes *IVb* and *Va* were also obtained by direct reaction of the butenal *II* and/or the dimer *VIa* with ethylene glycol in the presence of sulphuric acid.

In the cleavage by acetyl chloride, the oxetane *I* reacted only in the presence of concentrated sulphuric acid; the reaction was rapid and gave, instead of the expected 3-chloroalkyl esters[6,7], a mixture of products, the main one being 1-chloro-2,2-difluoro-3-methyl-3-butenyl acetate (*IVd*). Of the other components we identified 2,2-difluoro-3-methyl-3-butenylidene diacetate (*IVe*), butenal *II*, 3-acetoxy-2,2-difluoro-3-methylbutanal (*IIId*) and 1,2,2-trifluoro-3-methyl-3-butenyl acetate (*IVc*). In an analogous reaction in the system sulphuric acid-acetanhydride we also isolated (in addition to the diacetate *IVe* and acetate *IVc*) 3-acetoxy-2,2-difluoro-3-methylbutylidene diacetate (*Vd*). The possible formation of the acetate *IVd* and diacetate *IVe* by direct addition of acetyl chloride or acetanhydride to the intermediary butenal *II* under the conditions of the reaction was verified by comparison experiments. We believe that the triacetate *Vd* arose from acetylation of the monomeric hydroxyaldehyde *IIIa*, because acetylation of the cyclic dimer *VIa* under comparable reaction conditions led to the acetylated dimer *VIb* only. The data on composition of the reaction mixtures are compiled in Table I.

Further we dealt with catalytic cleavage of the oxetane *I* in gaseous phase by polyphosphoric acid on a support. At lower temperatures (150–160°C) the reaction took a clear-cut course; the product was butenal *II*, along with the unreacted starting

compound (32% conversion). However, an attempt to raise the conversion by elevating the reaction temperature to above 180°C and by extending the reaction time led to a mixture containing butenal *II* (61%), 1,1,5,5-tetrafluoro-2,6-dimethyl-1,6-heptadiene-4-ol (*IX*, 13%) and its formate (*X*, 26%). As it is indicated in Scheme 2, the formation of the alcohol *IX* and its formate *X* was evidently due to pyrolysis of the oxetane *I*, as had been the case before in similar experiments[8,9]. We suppose that the elimina-



SCHEME 2

TABLE I

Cleavage products (%, w/w) of 3,3,4-trifluoro-2,2-dimethyloxetane as determined by GLC

Agent	*II*	*IIId*	*IV*	*V*	*VIa*	*VII*	*VIII*
H_2SO_4/H_2O	20	—	—	—	66	—	—
H_3PO_4/H_2O	62	—	—	—	12	—	—
$(HPO_3)x$	95	—	—	—	—	—	—
HCl/H_2O	45	—	—	30[a]	5	—	15
HBr/H_2O	48	—	—	17[b]	24	—	—
H_2SO_4/CH_3OH	—	—	—	—	—	13[c]	—
HCl/CH_3OH	20	—	31[d]	27[a]	—	—	—
$H_2SO_4/(CH_2OH)_2$	—	—	62[e]	38[f]	—	—	—
H_2SO_4/CH_3COCl	3	2	71[g] + 19[h] + 0·5[i]	—	—	—	—
$H_2SO_4/(CH_3CO)_2O$	—	—	47[h] + 29[i]	24[j]	—	—	—

[a] *Vb*; [b] *Vc*; [c] after isolation; [d] *IVa*; [e] *IVb*; [f] *Va*; [g] *IVd*; [h] *IVe*; [i] *IVc*; [j] *Vd*.

tion of formyl fluoride produces olefin *Ic*, which adds to the carbonyl groups of the butenal *II*, and the resulting alcohol *IX* is then partially formylated to the ester *X*.

Isolation of the unsaturated aldehyde *II* and hydroxyaldehyde *IIIa* by distillation of the reaction mixture is rather difficult, since both compounds are unstable in the monomeric state. Depolymerization and re-polymerization of the two products interfere with the distillation, which makes the separation difficult. A freshly distilled sample of the butenal *II* had an ^{1}H NMR signal (CH=O) 9·32 ppm, which faded out with time and the original liquid solidified to a wax, the mean molecular mass of which (1 150), determined osmometrically, approximately corresponded to a decamer. Similarly, heating of the cyclic dimer *VIa* led to dissociation, so that it distilled in the monomeric form. Immediately after cooling the distillate was a viscous liquid, having an ^{1}H NMR residual signal (CH=O) 9·46 ppm, which disappeared on crystallization. Therefore, we tried to isolate the aldehydic products of the acid-induced cleavage with a solution of sodium hydrogen sulphite. However, the expected aldehyde-bisulphite was formed only from the aldehyde hydrate *Vb*. Neither the butenal *II* nor the dimer *VIa* formed such adducts, but the reactions with 2,4-dinitrophenylhydrazine and hydroxylamine gave the corresponding hydrazones and oximes.

EXPERIMENTAL

The temperature data are not corrected. The infrated spectra of solid substances (unless otherwise specified) were measured employing an apparatus Perkin Elmer, Model 325. The NMR spectra were measured in deuteriochloroform with an apparatus Varian XL-100, tetramethylsilane (for ^{1}H NMR) and $CFCl_3$ (for ^{19}F NMR) being used as internal standards. The mass spectra were measured with an apparatus Gas Chromatograph – Mass Spectrometer LKB 9000. The gas-chromatographic analyses were carried out using an apparatus Chrom III with the FID detection, the carrier gas being nitrogen. The stationary phases (poly(propylene sebacate), 1,4-butanediol succinate SE-30) were anchored to Chromaton N-AW. The molecular mass of the polymer in toluene at 50°C was determined with an apparatus Hitachi Elmer Perkin Mo. 115 Vapour Pressure Osmometer. The elemental analyses of the products are given in Table II.

Cleavage of 3,3,4-Trifluoro-2,2-dimethyloxetane (*I*)

A) *By* 80% *sulphuric acid*: To a mixture of *I* (100 g, 0·71 mol) and silica gel (20 g) was added, under stirring and cooling with ice, 80% sulphuric acid (200 g) in the course of 20 min. The mixture was then stirred at 20–30°C for 8 h. Ice-cold water (300 ml) was added, the remaining silica gel was filtered off, and the filtrate was extracted with ether (6 × 50 ml). The combined ethereal extracts were washed with a saturated aqueous solution of sodium hydrogen carbonate and water, and dried with magnesium sulphate. The ether was distilled off over a Vigreaux column: yield 68·9 g of the crude product which was analysed by gas chromatography and rectified.

2,2-*Difluoro*-2-*methyl*-3-*butenal* (II, 20% of the crude reaction mixture according to GLC) was obtained as a fraction boiling at 77–80°C (13·3 g), rapidly polymerizing into a waxy substance. IR spectrum (chloroform, cm^{-1}): $\nu(OH)_{bound}$ 3 550 w, $\nu(CH_2=)$ 3 100 w, $\nu(CH_3)$ 2 980 m.

TABLE II
Elemental analyses

Compound	Formula (mol.mass)	Calculated/Found				
		% C	% H	% Br	% Cl	% F
II	$C_5H_6F_2O$	49·98	5·04	—	—	31·65
	(120·1)	49·86	5·04			31·28
IIId	$C_7H_{10}F_2O_3$	46·64	5·60	—	—	21·09
	(180·1)	46·72	5·60			21·40
IVa	$C_7H_{12}F_2O_2$	50·57	7·28	—	—	22·88
	(166·1)	50·66	7·54			22·52
IVb	$C_7H_{10}F_2O_2$	51·18	6·15	—	—	23·15
	(164·1)	51·32	6·19			23·05
IVc	$C_7H_9F_3O_2$	46·13	4·98	—	—	31·30
	(182·1)	46·49	5·00			31·52
IVd	$C_7H_9ClF_2O_2$	42·37	4·57	—	17·86	19·14
	(198·5)	42·89	4·74		18·05	19·19
IVe	$C_9H_{12}F_2O_4$	48·63	5·44	—	—	17·11
	(222·1)	48·73	5·48			16·93
Va	$C_7H_{12}F_2O_3$	46·12	6·64	—	—	20·87
	(182·1)	46·14	6·68			21·10
Vb	$C_5H_9ClF_2O_2$	34·38	5·19	—	20·31	21·77
	(174·5)	34·41	5·29	—	20·36	21·87
Vc	$C_5H_9BrF_2O_2$	27·40	4·15	36·48	—	17·35
	(219·0)	27·91	4·03	36·17		17·47
Vd	$C_{11}H_{16}F_2O_6$	46·79	5·71	—	—	13·47
	(282·1)	46·68	5·84			13·95
VIa	$C_{10}H_{16}F_4O_4$	43·46	5·84	—	—	27·52
	(276·1)	43·66	5·82			27·17
VII	$C_{11}H_{16}F_4O_3$	48·51	5·93	—	—	27·93
	(272·1)	49·10	6·00			27·40
VIII	$C_5H_7ClF_2O$	38·34	4·51	—	22·65	24·28
	(156·5)	38·99	4·64		22·83	24·48
IX	$C_9H_{12}F_4O$	50·92	5·70	—	—	35·83
	(212·1)	50·65	5·95			35·30
X	$C_{10}H_{12}F_4O_2$	49·98	5·04	—	—	31·65
	(240·1)	49·68	5·14			31·28

^{1}H NMR spectrum (δ ppm): 1·82 (s, 3 H, CH_3—), 4·90–5·55 (b, 3 H, CH_2=, —CH—). ^{19}F NMR spectrum (σ ppm): 115·0 (m, 2 F, —CF_2—). Mass spectrum (*m/e* (relative intensity, %)): 65/100, 91/98, 39/54, 41/41, 51/30, 77/28, 92/17, 71/13, 46/11, 53/10; M^+ 120/6. 2,4-Dinitrophenylhydrazone: m.p. 126–128°C. The mean molecular mass of the polymer, measured osmometrically after several weeks' standing, was 1 150.

5,5-*Difluoro*-2-(1,1-*difluoro*-2-*hydroxy*-2-*methylpropyl*)-4-*hydroxy*-6,6-*dimethyl*-1,3-*dioxan* (*VIa*, 66% of the crude reaction product by GLC) was obtained as a fraction boiling at 130–140°C (23·6 g) which crystallized in several days, m.p. 93–95°C. IR spectrum (tetrachloromethane, cm^{-1}): $\nu(OH)_{free}$ 3 560 s, $\nu(OH)_{bound}$ 3 280 s, $\nu(CH_3)$ 3 920 m. ^{1}H NMR spectrum (hexadeuterioacetone, δ ppm, *J* Hz): 1·35 (m, 9 H, 3 × CH_3), 1·64 (s, 3 H, CH_3—), 4·06 (s, 1 H, —OH), 5·32 (dd, 1 H, —CH—OH), 5·78 (t, $^3J_{HF}$ = 8, 1 H, —CH—), 6·85 (d, $^3J_{HH}$ = 5, 1 H, HO—CH). ^{19}F NMR spectrum (hexadeuterioacetone, ppm, *J* Hz): 117·8, 125·0 (AB system, $^2J_{FF}$ = 255, 2 F, CF_2), 121·9, 123·5 (AB system, 2 F, CF_2). Mass spectrum (*m/e* (rel. intensity, %)): 59/100, 43/59, 92/30, 31/29, 47/21, 77/16, 41/16, 29/15, 65/13, 80/9, $(M-17)^+$ 259/0·02. 2,4-Dinitrophenylhydrazone: m.p. 156–158°C.

B) *Cleavage by* 85% *phosphoric acid*: a mixture of *I* (20 g, 0·14 mol), 85% phosphoric acid (40 ml) and silica gel (5 g) was stirred at 70°C for 7 h. After cooling it was diluted with water (100 mol), and 30% aqueous sodium hydroxide (65 ml) was added. The mixture was then extracted with ether (4 × 35 ml). The combined extracts were washed with a solution of sodium hydrogen carbonate and dried with magnesium sulphate. Distillation to remove the ether left 5·9 g of the crude product, which was shown (by GLC) to contain the butenal *II* (62%) and dioxan *VIa* (12%). Their identities were corroborated chromatographically with the aid of authentic samples.

C) *Cleavage by polyphosphoric acid*: a mixture of *I* (20 g, 0·14 mol), polyphosphoric acid (20 g) and silica gel (5 g) was stirred at room temperature for 20 h. After standing for 2 days it was diluted with water (30 ml) and worked up as in the preceding experiment; yield 8·3 g of a product containing 95% of *II* (GLC).

D) *Cleavage by hydrochloric acid*: a mixture of *I* (50 g, 0·34 mol), 35% hydrochloric acid (100 ml) and silica gel (26 g) was stirred at 40–60°C for 14 h, cooled, diluted with water (150 ml) and extracted with ether (3 × 30 ml). The combined ethereal extracts were washed with a solution of sodium hydrogen carbonate, dried with sodium carbonate and distilled to remove the ether; yield 33·5 g of a product containing 45% of *II*, 30% of *Vb*, 15% of *VIII*, 4% of *VIa*, and 3% of *I* (GLC).

3-*Chloro*-2,2-*difluoro*-3-*methyl*-1,1-*butanediol* (Vb) was isolated by gas chromatography as the constituent with a shorter retention time, m.p. 58–60°C. IR spectrum (KBr pellet, cm^{-1}): $\nu(OH)_{bound}$ 3 400 s, 3 330 s, $\nu(CH_3)$ 2 980 w, $\delta(CH_3)$ 1 460 m. ^{1}H NMR spectrum (hexadeuteriodimethyl sulphoxide, δ ppm): 1·66 (s, 6 H, 2 × CH_3), 4·98–5·30 (m, 1 H, CH), 6·65 (s, 1 H, OH), 6·72 (s, 1 H, OH). ^{19}F NMR spectrum (hexadeuteriodimethyl sulphoxide, δ ppm, *J* Hz): 119·7 (d, $^3J_{HF}$ = 8, 2 F, CF_2). Mass spectrum (*m/e* (relative intensity, %)): 92/100, 77/95, 47/51, 41/39, 65/37, 29/25, 39/19, 18/17, 51/14, $(M-18)^+$ 156/0·2. 2,4-Dinitrophenylhydrazone: m.p. 132–133°C.

4-*Chloro*-3,3-*difluoro*-2,2-*dimethyloxetane* (*VIII*) was isolated by gas chromatography as the constituent with the longer retention time. IR spectrum (cm^{-1}): $\nu(CH_3)$ 2 980 s, 2 995 s, $\delta(CH_3)$ 1 465 s, $\delta(CH_3)_{gem}$ 1 365 s, 1 390 s, ν(C—Cl) 720 s. ^{1}H NMR spectrum (1 ppm): 1·49 (s, 3 H, CH_3), 1·62 (s, 3 H, CH_3), 6·15–6·32 (m, 1 H, CHCl). ^{19}F NMR spectrum (δ ppm): 113·9, 117·1 (AB system, $^2J_{FF}$ = 195, $^3J_{HF}$ = 8, 2 F, CF_2). Mass spectrum (*m/e* (relative intensity, %)): 43/100, 65/63, 92/62, 78/56, 58/31, 39/27, 41/24, 98/24, 93/21, 47/19, $(M-35)^+$ 121/4·7.

E) *Cleavage by hydrobromic acid*: a mixture of *I* (40 g, 0·29 mol), 49% hydrobromic acid (80 ml) and silica gel (20 g) was stirred at 60—70°C for 7 h, then worked up as in the analogous cleavage with hydrochloric acid. GLC showed the product (31·8 g) to contain *II* (48%), *VIa* (24%), and *Vc* (17%).

3-*Bromo*-2,2-*difluoro*-3-*methyl*-1,1-*butanediol* (Vc) was isolated by preparative gas chromatography. IR spectrum (cm^{-1}): $\nu(OH)_{bound}$ 3 450 s, $\nu(CH_3)$ 2 960 s, $\delta(CH_3)$ 1 465 m, $\delta(CH_3)_{gem}$ 1 375, 1 395 m. ^1H NMR spectrum (hexadeuteriodimethyl sulphoxide, δ ppm): 1·23 (s, 6 H, 2 × CH_3), 5·00—5·56 (m, 1 H, CH), 8·30—8·54 (m, 2 H, 2 × OH). ^{19}F NMR spectrum (δ ppm): 118·0 (m, 2 F, CF_2). Mass spectrum (*m/e* (relative intensity, %)): 92/100, 65/94, 77/50, 126/49, 41/48, 39/44, 47/41, 93/39, 53/36, 51/26, $(M-18)^+$ 201/1·6. 2,4-Dinitrophenylhydrazone: m.p. 126—127°C.

F) *Cleavage by hydrogen chloride in methanol*: a solution of *I* (20 g, 0·14 mol) in methanol (50 ml) was saturated with hydrogen chloride and the mixture was left standing at room temperature for a fortnight. It was then filtered and distilled over a column to remove the methanol. GLC of the residue (19·7 g) determined 31% of *IVa*, 27% of *Vb*, and 20% of *II*.

2,2-*Difluoro*-3-*methyl*-3-*butenal dimethyl acetal* (IVa) was isolated by gas chromatography as the constituent with a medium retention time. IR spectrum (cm^{-1}): $\nu(CH_2{=})$ 3 100 w, $\nu(CH_3)$ 2 950 s, $\nu(CH_3O)$ 2 840 s, $\nu(C{=}C)$ 1 655 w, $\delta(CH_2)$ 1 465. ^1H NMR spectrum (δ ppm, *J* Hz) 1·88 (s, 3 H, CH_3), 3·52 (s, 6 H, 2 × CH_3O), 4·40 (t, $^3J_{HF}$ = 6, 1 H, CH), 5·20—5·45 (m, 2 H, $CH_2{=}$). ^{19}F NMR spectrum (δ ppm): 111·6 (m, 2 F, CF_2). Mass spectrum (m/*e* (relative intensity, %)): 75/100, 47/28, 31/16, 39/8, 103/7, 41/6, 85/6, 85/5, 65/5, 51/5, M^+ 166/0·05.

5,5-*Difluoro*-2-(1,1-*difluoro*-2-*methyl*-2-*propenyl*)-4-*methoxy*-6,6-*dimethyl*-1,3-*dioxan* (VII): to a stirred and cooled mixture of *I* (50 g, 0·36 mol), methanol (50 ml), and silica gel was added dropwise concentrated sulphuric acid (50 g) in the course of 20 min. The mixture was brought to the boil and kept at this temperature for 8 h. After cooling it was neutralized with solid sodium hydrogen carbonate and steam-distilled. The oily residue was extracted with ether (5 × 75 ml), the combined extracts were washed with water and dried with magnesium sulphate. The ether was distilled off and the oily residue (11·9 g) was rectified; yield 6·2 g (13%) of *VII*, b.p. 116 to 120°C/3·3 kPa, m.p. 46—48°C. IR spectrum (tetrachloromethane, cm^{-1}): $\nu(CH_2)$ 3 020 w, (CH_3) 2 947 w, (CH_3) 1 430—1 480 m. ^1H NMR spectrum (δ ppm, *J* Hz): 1·35 (m, 3 H, CH_3), 1·53 (m, 3 H, CH_3), 1·90 (m, 3 H, $CH_3{-}C{=}C$), 3·55 (s, 3 H, CH_3O), 4·88 (d, $^3J_{HF}$ = 9, 1 H, $CH{-}{-}OCH_3$), 5·30 (m, 2 H, $CH_2{=}$), 5·46 (1 H, CH). ^{19}F NMR spectrum (δ ppm, *J* Hz): 111·8, 113·3 (AB system, $^2J_{FF}$ = 260, 2 F, CF_2), 117·0, 125·5 (AB system, $^2J_{FF}$ = 260, 2 F, CF_2). Mass spectrum (*m/e* (relative intensity)): 94/100, 61/98, 92/89, 135/61, 43/52, 65/39, 181/38, 77/38, 33/36, 59/30.

G) *Cleavage by sulphuric acid in ethylene glycol*: to a mixture of *I* (25 g, 0·18 mol), ethylene glycol (25 g) and silica gel (10 g) was slowly added dropwise concentrated sulphuric acid (25 g) under stirring. The mixture was heated to 80°C for 7 h, cooled, diluted with water (50 ml), filtered and extracted with ether (4 × 25 ml). The combined extracts were washed with water, a saturated solution of sodium hydrogen carbonate and dried with magnesium sulphate. The ether was removed and the crude product was distilled *in vacuo*; yield 16·2 g of an oil boiling at 60 to 150°C/2·1 kPa and containing 62% of *IVb* and 38% of *Va* (GLC).

2-(1,1-*Difluoro*-2-*methyl*-2-*propenyl*)-1,3-*dioxolane* (IVa) was obtained by gas chromatography of the distillate as the component with a shorter retention time, b.p. 75—77°C/4·2 kPa. IR spectrum (cm^{-1}): $\nu(CH_3)$ 2 955 m, $\nu(C{=}C)$ 1 650 w, $\delta(CH_2)$ 1 470 w, $\delta(CH_3)$ 1 455 m. ^1H NMR spectrum (δ ppm): 1·88 (s, 3 H, CH_3), 4·03 (m, 4 H, CH_2CH_2), 5·14 (t, $^3J_{HF}$ = 8, 1 H, CH), 5·30 (d, 2 H, $CH_2{=}$). ^{19}F NMR spectrum (δ ppm): 116·0 (d, 2 F, CF_2). Mass spectrum (*m/e*

(relative intensity,%)): 73/100, 45/45, 39/6, 65/5, 43/5, 74/4, 91/3, 41/3, 119/2, 51/2, $(M-1)^+$ 163/0·2.

2-(1,1-*Difluoro*-2-*hydroxy*-2-*methylpropyl*)-1,3-*dioxolane* (Va) was obtained by gas chromatography of the distillate as the component with a longer retention time, boiling at 112—115°C/3·2 kPa. IR spectrum (cm^{-1}): $\nu(OH)_{bound}$ 3 460 s, $\nu(CH_3)$ 2 990 s, $\nu(CH_2)$ 2 905 s, $\delta(CH_2)$ 1 470 m, $\delta(CH_3)_{gem}$ 1 360, 1 330 m. ^1H NMR spectrum (δ ppm, J Hz): 1·35 (s, 6 H, 2× CH_3), 2·72 (s, 1 H, OH), 4·03 (m, 4 H, CH_2CH_2), 5·33 (t, $^3J_{HF} = 9$, 1 H, CH). ^{19}F NMR spectrum (σ ppm): 114·9 (d, 2 F, CF_2). Mass spectrum (*m/e* (relative intensity, %)): 73/100, 45/30, 43/17, 57/13, 58/9, 74/4, 124/3, 102/3, 41/2, M^+ 180/0·04.

H) *Cleavage by sulphuric acid in acetyl chloride*: to a mixture of *I* (250 g, 1·78 mol) and silica gel (25 g) was added dropwise, under stirring and cooling, a solution of sulphuric acid (90 ml) in acetyl chloride (355 ml; 5 mol) in the course of 1 h, in such a way that the temperature did not exceed 7°C. The mixture, at first strongly effervescent with the evolving gases, was left standing at room temperature for 36 h, then diluted with ether (300 ml) and poured into ice (300 g). The acidity of the mixture was neutralized with a 30% solution of sodium hydroxide (300 ml), the ethereal layer was separated and the aqueous layer was extracted with ether (4 × 75 ml). The combined ethereal portions were washed with water and aqueous sodium hydrogen carbonate, then dried with magnesium sulphate. The ether was distilled off and the residue (342 g) was analysed by GLC; it was found to contain 71% of *IVd*, 19% of *IVe*, 3% of *II*, 2% of *IIId*, and 0·5% of *IVc*. The mixture was resolved by rectification under reduced pressure.

1-*Chloro*-2,2-*difluoro*-3-*methyl*-3-*butenyl acetate* (IVd) was obtained by the rectification as a fraction (243 g) boiling at 68—70°C/1·9 kPa. IR spectrum (cm^{-1}): $\nu(CH_2=)$ 3 100 w, $\nu(CH_3)$ 2 980 m, $\nu(C=O)$ 1 780 s, $\nu(C=C)$ 1 650 w, $\delta(CH_3)$ 1 450 m. ^1H NMR spectrum (δ ppm, J Hz): 1·90 (s, 3 H, CH_3), 2·18 (s, 3 H, CH_3CO), 5·45 (d, $^2J_{HH} = 13$, 2 H, $CH_2=$), 6·60 (t, $^3J_{HF} = 8$, 1 H, CH). ^{19}F NMR spectrum (δ ppm): 110·0, 115·5 (AB system, $^2J_{FF} = 250$, 2 F, CF_2). Mass spectrum (*m/e* (relative intensity, %)): 43/100, 92/5, 39/3, 91/3, 44/3, 65/2, 41/2, 107/1, 42/1, M^+ 198, 0·07.

3-*Acetoxy*-2,2-*difluoro*-3-*methylbutanal* (IIId) was obtained by gas chromatography of the fraction boiling at 83—86°C/7·2 kPa. IR spectrum (cm^{-1}): $\nu(CH_3)$ 2 950 w, $\nu(C=O)$ 1 750 s, $\delta(CH_3)$ 1 460 m, $\delta(CH_3)_{gem}$ 1 385, 1 365s. ^1H NMR spectrum (δ ppm): 1·65 (s, 6 H, 2× CH_3), 2·04 (s, 3 H, CH_3CO), 9·52 (m, 1 H, CH=O). ^{19}F NMR spectrum (δ ppm): 126·5 (m, 2 F, CF_2). Mass spectrum (*m/e* (relative intensity, %)): 92/100, 59/97, 43/69, 65/61, 77/56, 61/53, 101/47, 91/33, 41/22, 39/19, $(M+1)^+$ 181/0·56. Dinitrophenylhydrazone: m.p. 158—159°C.

I) *Cleavage by sulphuric acid in acetanhydride*: to a mixture of *I* (50 g, 0·38 mol) and silica gel (20 g) was added dropwise, under stirring and cooling, a solution of concentrated sulphuric acid (18·5 ml) in acetanhydride (102 g, 1 mol) during 1 h. The mixture was stirred 8 h at room temperature, left standing overnight and poured onto ice (200 g). The remaining silica gel was filtered off and the filtrate was extracted with ether (5 × 30 ml). The combined extracts were washed with water, aqueous sodium hydrogen carbonate, and dried with magnesium sulphate. The ether was removed and the residue (55 g) was analysed by GLC; it contained 47% of *IVa*, 29% of *IVc*, and 24% of *Vd*. This mixture was resolved by rectification under reduced pressure.

1,2,2-*Trifluoro*-3-*methyl*-3-*butenyl acetate* (IVc) was obtained by the rectification as a fraction boiling at 48—49°C/1·9 kPa. IR spectrum (cm^{-1}): $\nu(CH_2=)$ 3 100 w, $\nu(CH_3)$ 2 980 w, $\nu(C=O)$ 1 785 s, $\delta(CH_3)$ 1 375 s, ^1H NMR spectrum (δ ppm, J Hz): 1·91 (s, 3 H, CH_3), 2·19 (s, 3 H, CH_3CO), 5·41 (d, $^2J_{HH} = 11$, 2 H, $CH_2=$), 6·29 (dt, $^2J_{HF} = 53$, $^3J_{HF} = 6$, 1 H, CHF). ^{19}F NMR spectrum (δ ppm): 115·6 (AB system, $^2J_{FF} = 270$, 2 F, CF_2), 147·5 (m, 1 F, CHF). Mass spectrum (*m/e* (relative intensity, %)): 43/100, 91/14, 39/12, 44/8, 134/7, 65/6, 41/5, 42/5, 51/4, 59/4, M^+ 182/0·48.

2,2-*Difluoro*-3-*methyl*-3-*butenylidene diacetate* (IVe) was obtained by gas chromatography of the fraction boiling at 114—118°C/2·9 kPa. IR spectrum (cm^{-1}): $\nu(CH_2=)$ 3 100 w, $\nu(CH_3)$ 2 980 w, $\nu(C=O)$ 1 775, 1 785 s, $\delta(CH_3)$ 1 370 s. ^1H NMR spectrum (hexadeuterioacetone, δ ppm, J Hz): 1·88 (s, 3 H, CH_3), 2·10 (s, 6 H, 2× CH_3CO), 5·37 (d, $^2J_{HH} = 6$, 2 H, $CH_2=$), 7·00 (t, $^3J_{HF} = 7$, 1 H, CH). ^{19}F NMR spectrum (hexadeuterioacetone, δ ppm): 113·9 (m, 2 F, CF_2). Mass spectrum (*m/e* (relative intensity, %)): 43/100, 103/9, 91/3, 44/3, 134/2, 65/2, 61/2, 39/2, 42/1, M^+ 222/0·75.

3-*Acetoxy*-2,2-*difluoro*-3-*methylbutylidene diacetate* (Vd), b.p. 153°C/2·0 kPa, was obtained by gas chromatography of the fraction boiling in the range 106—150°C/1·6 kPa. IR spectrum (cm^{-1}): $\nu(CH_3)$ 3 000 m, $\nu(C=O)$ 1 740—1 790 s, $\delta(CH_3)$ 1 370 s. ^1H NMR spectrum (hexadeuterioacetone, δ ppm, J Hz): 1·65 (s, 6 H, 2× CH_3), 1·98 (s, 3 H, CH_3CO), 2·13 (s, 6 H, 2× CH_3CO), 7·29 (t, $^3J_{HF} = 9$, 1 H, CH). ^{19}F NMR spectrum (δ ppm, hexadeuterioacetone): 124·1 (m, 2 F, CF_2). Mass spectrum (*m/e* (relative intensity, %)): 43/100, 103/16, 92/10, 61/5, 101/4, 59/4, 44/3, 181/2, 77/2, 42/1, $(M-60)^+$ 222/0·9.

Catalytic Cleavage of *I* in Gaseous Phase

a) The oxetane *I* (14 g, 0·1 mol) was evaporated (in the course of 40 min) and the vapour was introduced into a column (length 15 cm, I.D. 12 mm) packed with polyphosphoric acid on glass wool. The temperature in the column was kept in the range 150—160°C. In the adjoining freezing trap, chilled with dry ice, there condensed 11·5 g of a mixture composed of *II* (32%) and *I* (68%); this composition was determined by GLC with the aid of authentic samples.

b) The oxetane *I* (14 g, 0·1 mol) was evaporated, in the course of 15 min, with a stream of nitrogen (50 ml min^{-1}) and introduced into a teflon column (length 260 cm, I.D. 6 mm, packed with earthenware grains 0·35—0·45 mm impregnated with 10% polyphosphoric acid) heated to 170 to 180°C; 10 g of the crude product condensed in the freezing trap and then polymerized exothermically at room temperature to a wax-like substance (8·2 g). This was heat-depolymerized under reduced pressure (1·7 kPa) to 6·1 g of a distillate, which was found by GLC to be composed of *II* (61%), *IX* (13%), and *X* (26%).

1,1,5,5-*Tetrafluoro*-2,6-*dimethyl*-1,6-*heptadiene*-4-*ol* (IX) was isolated by gas chromatography from the distillate (after the depolymerization) as the component with a longer retention time. IR spectrum (cm^{-1}): $\nu(OH)_{free}$ 3 580 w, $\nu(OH)_{bound}$ 3 420, $\nu(CF_2=)$ 1 760 s. ^1H NMR spectrum (δ ppm, J Hz): 1·65 (m, 3 H, CH_3), 1·89 (s, 3 H, CH_3), 1·95—2·30 (b + m, 3 H, CH_2, OH), 3·73 (m, 1 H, CH), 5·31 (d, $^2J_{HH} = 13$, 2 H, $CH_2=$). ^{19}F NMR spectrum (δ ppm, J Hz): 94·7, 95·7 (AB system, $^2J_{FF} = 55$), 112·2, 114·3 (AB system, $^2J_{FF} = 245$, 2 F, CF_2). Mass spectrum (*m/e* (relative intensity, %)): 65/100, 91/88, 73/70, 92/65, 77/35, 53/28, 39/28, 101/26, 41/26, 43/25, $(M-20)^+$ 192/4.

1,1,5,5-*Tetrafluoro*-2,6-*dimethyl*-1,6-*heptadiene*-4-*yl formate* (X) was isolated as the component with a shorter retention time. IR spectrum (tetrachloromethane, cm^{-1}): $\nu(CF_2=)$ 1 765 s, $\nu(C=O)$ 1 740 s. ^1H NMR spectrum (δ ppm): 1·62 (m, 3 H, CH_3), 1·85 (s, 3 H, CH_3), 2·10 to 2·70 (m, 2 H, CH_2), 5·15—5·65 (m, 3 H, $CH_2=$, CH), 8·05 (s, 1 H, CH=O). ^{19}F NMR spectrum (δ ppm, J Hz): 93·6, 94·9 (AB system, $^2J_{FF} = 50$, 2 F, $CF_2=$), 110·8, 113·6 (AB system, $^2J_{FF} = 250$, 2 F, CF_2). Mass spectrum (*m/e* (relative intensity, %)): 91/100, 65/90, 73/78, 125/64, 194/36, 39/32, 41/31, 77/29, 53/25, 92/24.

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