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THE REACTION OF SOME 3- AND 4-FLUOROOXETANES WITH ACIDS*

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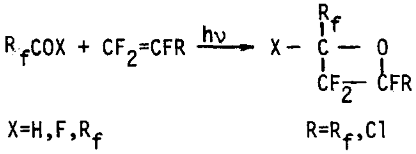
SUMMARY

Several oxetanes prepared from hexafluoroacetone and hydrofluoroolefins were treated with aluminum chloride. Substitution of fluorine by chlorine occured on the 3-and 4-carbon atoms as well as cleavage of the ether leakage to give chloroalkyl carbinols or in, some cases, vinyl carbinols. Individual samples of the cis and trans -3,4-difluorooxetanes formed roughly equivalent amounts of the 3-fluoro-4-chlorooxetane stereoisomers, indicating a common carbonium intermediate. Treatment of the 4-fluorooxetane with sulfuric acid gave a dioxetane, a dioxene and an unsaturated aldehyde.

INTRODUCTION

Oxetanes containing fluorine have been prepared by a variety of methods but the most important synthetic method involves the photoinitiated cycloaddition of a carbonyl compound to an olefin. Harris and Coffman [1] found that fluorine-containing aldehydes, ketones and acid fluorides reacted with a variety of perfluoroolefins to give polyfluorooxetanes.



$$R_fCOX + CF_2{=}CFR \xrightarrow{h\nu} X-C(R_f)\text{—}O-CFR-CF_2 \text{ (ring)}$$

$X{=}H,F,R_f$ $\quad$ $R{=}R_f,Cl$

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[*] Dedicated to Emeritus Professor W.K.R. Musgrave on the occasion of his 70th birthday.

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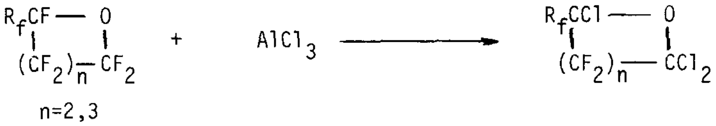
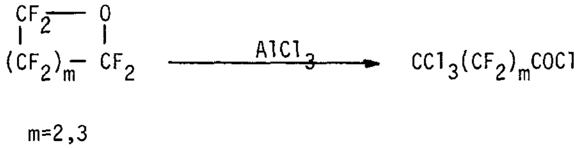
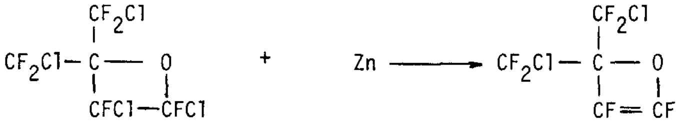
The polyfluorooxetanes were reported to exhibit considerable thermal stability [1]. Cyclic perfluoroethers were considered to be chemically inert until Tiers [2a] found that the α-fluorine atoms were replaced by chlorine at 150 -200°in the presence of $AlCl_3$.



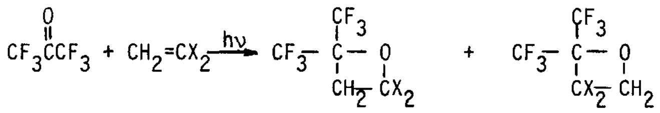
Ring opening occured with unsubstituted perfluorotetrahydrofurans and pyrans [2b] to form ω-trichloromethyl acid chlorides.



Wolff and his associates also noted the thermal stability of polyfluorooxetanes as well as their chemical inertness [3]. They found that the adduct from hexafluoroacetone and chlorotrifluoroethylene remained unchanged when refluxed for several hours with the following reagents; NaOH solution (50% by weight), sodium ethylate, PBr_3, HI and $AlCl_3$. However, they were able to obtain an oxetene by dechlorinating a 3,4-dichloroperhaloxetane [4].



Somewhat later Cook and Landrum described the cycloaddition of hexafluoroacetone to ethylene, vinyl fluoride and vinylidene fluoride [5]. They noted the formation of isomeric oxetanes from the fluoroolefins.

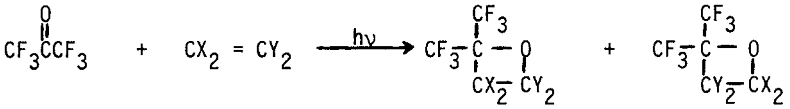


Since very little research has been carried out on the chemical properties of partially fluorinated oxetanes, it was decided to prepare a number of such compounds and study their reactions.

RESULTS AND DISCUSSION

The oxetanes studied were made by the ultraviolet induced addition of hexafluoroacetone to ethylene, vinyl fluoride, vinylidene fluoride, 1,2-difluoroethylene, trifluoroethylene, $CF_3CH{=}CH_2$ and butadiene as described [5]. As noted before,mixtures of positional isomers were usually obtained.

For example, $CF_3CH{=}CH_2$ formed (8)and (9) in a ratio of 2.4 : 1.



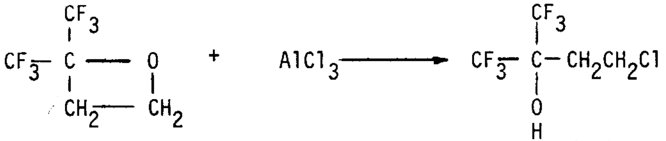
(2), (6) and (9) (3), (7) and (8)

(1) X=Y=H (2) X=H, Y=H,F (4-fluoro) (3) X=H, Y=H,F (3-fluoro) (4) X=Y=H,F (cis) (5) X=Y=H,F (trans) (6) X=H, Y=F (4-difluoro) (7) X=H, Y=F (3-difluoro) (8) X=H, Y=H, CF_3 (3-trifluoromethyl) (9) X=H, Y=H, CF_3 (4-trifluoromethyl) (10) X=H, Y=H, vinyl.

Stereoisomers were formed in some cases; for example 1,2-difluoroethylene gave cis and trans isomers which could be separated by distillation.

In our laboratory it was found that partially fluorinated oxetanes reacted with $AlCl_3$ so vigorously at room temperature that a solvent had to be used to control the reaction.

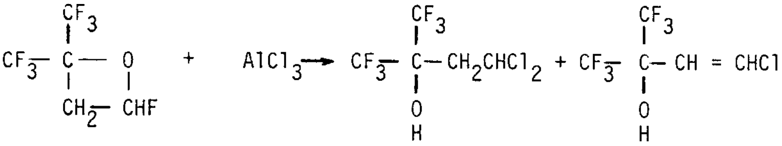
When the oxetane (1) from hexafluoroacetone and ethylene was heated with $AlCl_3$, a simple ring opening occurred and a good yield (45%) of the carbinol was obtained. No other product was isolated.



(1) (11)

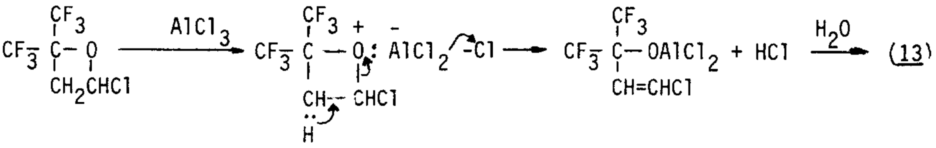
This compound was isolated previously from the reaction mixture of $AlCl_3$, ethylene and hexafluoroacetone [6].

When a single fluorine atom was present in the 4-position of the oxetane, replacement of fluorine by chlorine occurred with ring cleavage to give a saturated and unsaturated carbinol.

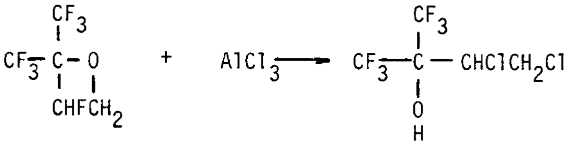


(2) (12) (13)

The formation of the vinyl carbinol can be explained by loss of a proton from the complexed chlorooxetane with simultaneous ring-opening.



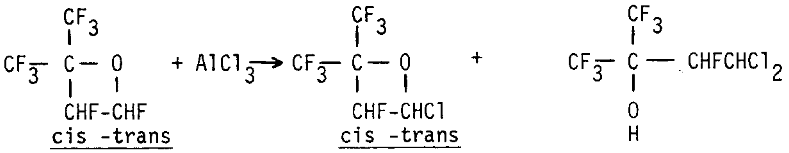
The isomeric 3-fluorooxetane reacted with $AlCl_3$ to give a single product, the dichloroethyl carbinol. No chlorooxetane nor vinyl carbinol was isolated.



(3) (14)

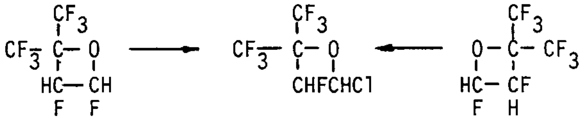
This is the only 3-fluorooxetane in which the fluorine was replaced by chlorine. No reaction occurred when the 3,4,4-trifluoro derivative was heated with aluminum chloride.

When fluorine atoms were present in both 3-and 4-positions, only replacement of the 4-fluorine occurred to give the two isomeric 4-chloro-3-fluoro derivatives as chief products along with a smaller amount of the ring opened product.



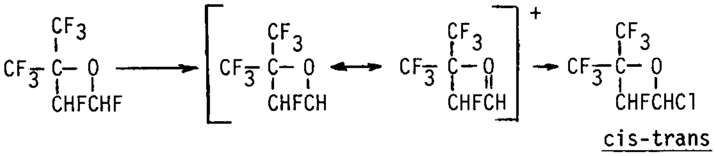
cis -trans (4) (5) — cis -trans (15) (16) — (17)

The starting difluorooxetanes were then separated and each allowed to react with $AlCl_3$ and almost equal amounts of the cis-trans- fluorochlorooxetanes were formed.



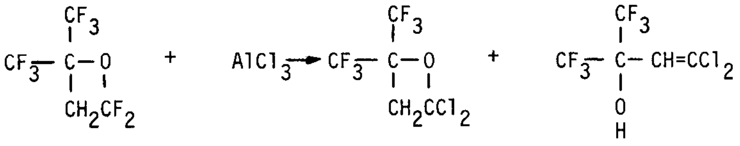
(4) — (15)(16) — (5)

This result suggests the presence of an intermediate carbonium ion.



cis-trans (15) (16)

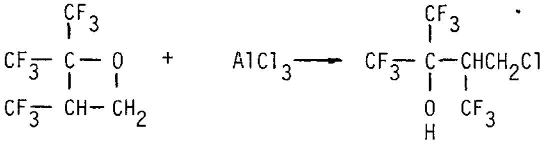
Both ring fluorine atoms were replaced in the 4,4-difluorooxetane (6) to give the dichlorooxetane and the dichlorovinyl carbinol.



(6) — (18) — (19)

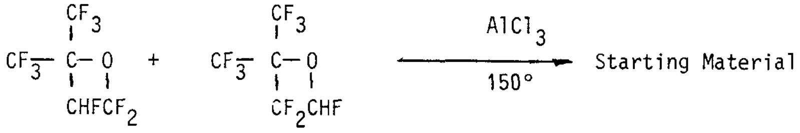
The second fluorine atom was more easily replaced than the first since only the dichloro derivatives were isolated.

When a trifluoromethyl group is present on the 3-carbon atom, simple ring opening occurs as shown below; (20) was obtained in 48% isolated yield.



(8) (20)

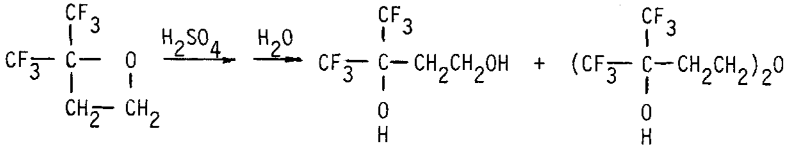
When a mixture of the two isomeric oxetanes shown below were heated with $AlCl_3$ for 12 hours at 150°, no significant reaction occurred and only starting material and trace amounts of any other material were isolated.



This result is some what unexpected since Hudlicky [7] has shown recently that cleavage of $C_2H_5OCF_2CHCFCl$ occurred in the presence of $AlCl_3$ at 100 ° to give ethyl chloride and CHFClCOCl, presumable via $CHFClCCl_2OC_2H_5$.

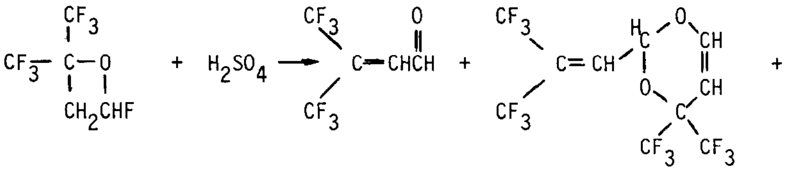
An attempt was made to promote ring opening with a mixture of 2,2-bis(trifluoromethyl)-3-fluorooxetane and the 4-fluoro isomer with potassium chloride and catalytic amounts of 18-crown-6 ether. However, no reaction was observed, indicating that a S_N2 mechanism is not involved in these reactions.

Sulfuric acid reacted with 2,2-bis(trifluoromethyl)oxetane to form the known 4,4,4-trifluoro-3-trifluoromethyl-1,3-butanediol (21) as the major product (30% yield) and the ether (22) derived from it in a 12% yield.

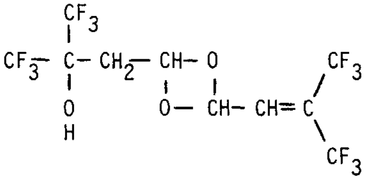


(1) (21) (22)

The 4-fluoro oxetane (2) also reacted with sulfuric acid and gave three compounds; 1) the unsaturated aldehyde 13%, (23); 2) a dioxene 22%, (24) and, as the major product 24%, a dioxetane (25).

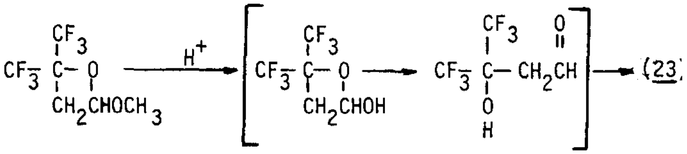


(2) (23) (24)



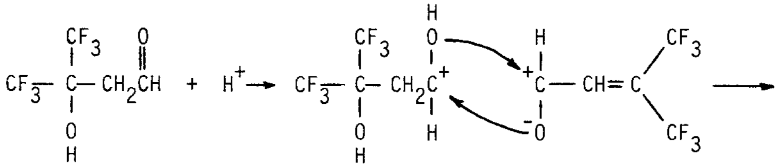
(25)

The unsaturated aldehyde had been made previously by the reaction of the cyclic acetal,shown below, with sulfuric acid [9].



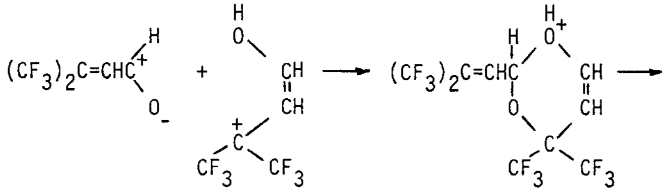
β-Hydroxy aldehydes lose water readily to become unsaturated but it is difficult to remove the hydroxy group from a carbon containing two trifluoromethyl groups so that the absence of any β-hydroxy aldehyde was surprising.

It seems probable that the β-hydroxy aldehyde was present in the reaction mixture since it is difficult to postulate a route to the chief product without its presence.


(25)

The dioxene can be accounted for by the cycloaddition of one unsaturated compound to another.

$$(CF_3)_2C{=}CHCHO + H^+ \rightarrow (CF_3)_2C{=}CH\overset{+}{C}HOH \leftrightarrow (CF_3)_2\overset{+}{C}CH{=}CHOH$$


(24)

EXPERIMENTAL

All temperatures are reported as observed. Infrared spectra were recorded with a Beckman IR8 double beam spectrophotometer. Proton nuclear magnetic spectra were taken on a Varian A60A spectrometer operating at 60 MHz with TMS as internal standard. Fluorine spectra were recorded on a Varian XL-100 spectrometer operating at 94.1 MHz with trifluoroacetic acid as a standard. Most of the mass spectra were run on a Hitachi Perkin - Elmer RMU-6E spectrometer and, where exact mass was required, a AEI - MS30 Double-beam, double-focusing spectrometer coupled to a computer was used.

Analytical gas chromatography was performed on an F and M 700 instrument using helium as carrier gas and a thermal detector. The column, 8' x $^1/_4$", was packed with 20% SE-30 on silanized, acid washed Chromasorb P, 30 - 60 mesh. All preparative work was done on a F and M Prepmaster using a 8' x $^3/_4$" column packed as described above.

Preparation of Oxetanes

In general oxetanes were prepared in an evacuated 3-necked 12 l flask equipped with a manometer, collection flask and a quartz well containing a 450 watt Hanovia high pressure mercury lamp. Equimolar amounts of hexafluoroacetone and the olefin were allowed to expand into the flask to 30 cm pressure and the lamp started. When the reaction was complete, the collection flask was removed and the contents of the reactor pumped through a liquid nitrogen trap. Data for oxetanes not previously reported are given.

Cis and Trans -2,2-Bis(trifluoromethyl)-3,4-difluorooxetane (4 and 5).

Equal volumes of hexafluoroacetone and 1,2-difluoroethene were admitted to a 12 l flask and irradiated for 18 hours. The liquid product (26.4g) was distilled to give 12.8 g of trans isomer and 8.5.g of cis isomer.

Trans-2,2-bis(trifluoromethyl)-3,4-difluorooxetane (5) had the following properties; b.p, 52-3°; ir (gas) cm^{-1} 3003 (C-H), 1408-96.6. m/e 211 (M$^+$ -F), 191 (M$^+$-HF$_2$), 182 (M$^+$-COHF), 163 (M$^+$-HF-COF), 113 (M$^+$-COHF-CF$_3$), 97(CF$_3$CO)$^+$, 69 (CF$_3$)$^+$, 64 (CHF = CHF)$^+$. Calcd: C, 26.10; H, 0.88. Found: C, 25.60; H, 0.83. ^{1}H; 5.28 (d,d,d, J= 2.50, 11.00, 50.50, 1H, CHFCHFO), 6.25 (d,d,d, J= 2.50, 6.00, 64.80, 1H, CHFCHFO). ^{19}F; -10.14 (d,q,d, J=2.60, 14.40, 8.8, 3F, CF$_3$), -5.94 (d,q,d, J=0.70, 1.80, 8.8, 3F, CF$_3$), 114.93 (d,q,d,d,q, J=2.60, 6.00, 50.50, 14.40, 1.80, 1F, CHFCHFO), 30.84 (d,d,q,d,q, J=2.60, 64.80, 11.00, 2.60, 0.70, 1F, CHFCHFO).

Cis-2,2-bis(trifluoromethyl)-3,4-difluorooxetane (4) had: B.p. 82-3°; ir (gas) cm^{-1} 3003 (C-H), 1400 - 1005, 710. The mass spectrum was nearly identical to that of the isomer. Found: C, 25.65; H, 0.87. ^{1}H; 5.28 (d,d,d, J=3.40, 8.10, 50.60, 1H, CHFCHFO), 6.25 (d,t, J=3.40, 66.60, 3.30, 1H, CHFCHFO). ^{19}F; -10.35 (d,q,d, J=6.40, 14.60, 9.10, 3F, CF$_3$), -5.89 (q,d,d, J=1.00, 1.65, 9.10, 3F, CF$_3$), 126.08 (d,q,d,d,q, J=5.60, 3.30, 50.60, 14.60, 1.65, 1F, CHFCHFO), 47.41 (d,d,q,d,q, J=66.60, 8.10, 6.40, 5.60, 1.00, 1F, CHFCHFO).

2,2,3- and 2,2,4-Tris(trifluoromethyl)oxetane (8 and 9).

Hexafluoroacetone and 3,3,3-trifluoropropene were irradiated 38 hours to give 132 g of product which was distilled to give 70 g of the oxetanes. They were separated by preparative glc and characterized.

2,2,3-Tris(trifluoromethyl)oxetane (8). B.p. 86°, ir (gas) cm^{-1} 3106, 2933 (C-H), 1401 - 936, 749, 719. m/e 2.61 (M+ -1), 241 (M^+ - H_2COF), 193 (M^+ - CF_3), 77 $(CF_2{=}CHFCH_2)^+$, 69 $(CF_3)^+$. ^1H; 4.17 (s,J = 8.5 1H,). (4.80, m, 2H,). ^{19}F, 2.42 (q, J = 10.0, 3F, CF_3), -3.35 (q,q,J = 10.0, 12.5, 3F, CF_3), -10.20 (d,q,J = 12.5, 8.5, 3F, CF_3CHCH_2). Calcd: C, 27.50; H,1.15. Fd: C 27.52; H, 1.16.

2,2,4-Tris(trifluoromethyl)oxetane (9). B.p. 94-5°, ir (gas) cm^{-1}: 1402 - 973, 7.5, 7.6, 7.7, 8.0, 8.18, 8.39, 8.58, 9.00, 9.25, 9.61, 9.79, 10.28, 692 m/e 261 (M^+ -1) 243 (M^+-F), 223 (M^+-HF_2), 193 (M^+-CF_3), 145 $[CF_3(CF_2)\,C = CH_2]^+$, 95 $(CF_3C{=}CH_2)^+$, 69 $(CF_3)^+$. Found: C, 27.57; H, 1.28 : ^1H; 3.15 (m, 2H) 5.07 (m, 1H).^{19}F; 1.12 (q,J = 8.5, CF_3). 2.61 (q, J = 5.0, 3F, $CHCF_3$).

2,2-Bis(trifluoromethyl)-3-vinyloxetane (10).

1,3-Butadiene (0.25m) and hexafluoroacetone (0.25m) were irradiated 55 hours and the products collected to give 14 g of liquid from which the oxetane was separated by preparative glc. The yield was estimated to be about 11%. ir (gas) cm^{-1} 3125 (=CH), 2964, 2914 (C-H), 1637 (C=), 1348 - 1033, 984, 890, 742, 706, 678. m/e 220 (M^+), 190 (M^+-HCHO), 121 (M^+-HCHO-CF_2), 101 (M^+-HCHO-CF_3-HF), 69 $(CF_3)^+$, 54 $(CH_2{=}CH - CH = CH_2)^+$. Calcd: C, 38.19; H, 2.75. Fd: C, 39.13; H, 2.80. ^{1}Hnmr: ^1H; 5.33 (m, 2H, 1H,=CH), 4.17 (q, J = 8.0, 1H, CH), 4.86 (m, 2H, CH_2), ^{19}F; -4.33 (q, d, J = 9.0, 2.0, 3F, CF_3), 0.87 (q, J = 9.0, 3F, CF_3).

Reactions of Oxetanes with Anhydrous Aluminum Chloride

Reaction of 2,2-Bis(trifluoromethyl)oxetane (1).

Aluminum chloride (0.102m) was added to a 200 ml, 3-necked flask containing 100 ml nitrobenzene and heated to 85°. The oxetane (0.093m) was added dropwise over a period of 35 minutes at 100°. The solution was steam-distilled directly from the flask and the organic layer separated and dried. Distillation yielded 1,1,1-trifluoro-2-hydroxy-2-trifluoromethyl-4-chlorobutane (11), (9.6g, 45% yield) at 102-3° (205 Torr), n^{25} 1.3498. Published[6]; B.p. 75° (175 Torr), n^{20} 1.3500, d^{20} 1.5541. Spectral data were gathered for additional proof of structure. ir(gas) cm^{-1} 3623, 3571 (O-H) 1299 - 1230 (C-F) 1183, 1149, 1124, 1098, 1036, 702, 651. m/e 213 (M^+-OH), 193 (M^+-H_2O,F), 161 (M^+-CF_3), 69 $(CF_3)^+$. ^1H; 2.38 (t, J=8.0, 2H, CH_2, 3.67 (t, J=8.0 2H ,CH_2Cl), 3.37 (s, OH). ^{19}F; -27.31 (s).

Reaction of 2,2-Bis(trifluoromethyl)-3-fluorooxetane (3).

The oxetane (0.09m) and $AlCl_3$ (0.2m) reacted for 2.5 hours at 85-90° to give a 12.5% yield of 1,1,1-trifluoro-2-hydroxy-2-trifluoromethyl-3,4-dichlorobutane (14).

B.p. 78-80° (87.5 Torr), n^{25} 1.3766. ir(gas) cm^{-1} 3636, 3559, (O-H), 1000 - 1333 (C-F), 697. m/e 229 (M^+-Cl), 211 (M^+-HCl-OH), 195 (M^+-CF_3), 159 (M^+-CF_3-HCl), 69 (CF_3).$^+$ Calcd: C, 22.66; H, 1.52. Fd:C, 22.30; H, 1.58. ^1H; 4.15 (m, CHCl), 3.72 (m, 2H), 3.88 (s,OH). ^{19}F -13.86 (q, J=9.0, CF_3), -14.86 (q, J=9.0, CF_3).

Reaction of 2,2-Bis(trifluoromethyl)-4-fluorooxetane (2).

Using the procedure described above, $AlCl_3$ (0.2m) and the oxetane (0.1m) gave a 10% yield of (13) and a 27% yield of (12).

1,1,1-Trifluoro-2-hydroxy-2-trifluoromethyl-2,2,2-trifluoro-4,4-dichlorobutane (12). B.p. 79-81°(80 Torr.). ir (gas) cm^{-1}: 3584 (OH), 1000-1333, (C-F), 789, 704, 645. m/e 264 (M^+), 249(M^+-F), 228, (M^+-HCl), 194, (M^+-HCF_3), 176, (M^+-CF_4), 69, (CF_3).$^+$ Calcd: C, 22.66; H, 1.52; Cl, 26.76. Fd: C, 22.67; H, 1.42; Cl, 26.47. ^1H; 2.97, (d, J=6.0, 2H), 6.05, (t, J=6.0, 1H), 3.73, (s, 1H OH). ^{19}F; -0.70 (s,6F).

1-Chloro-3-hydroxy-4,4,4-trifluoro-3-trifluoromethylbutene-1 (13). B.p. 88°, (175 Torr.). Calcd: C, 26.28; H, 1.32; Cl, 15.51. Fd: C, 25.90; H 1.37; Cl, 15.31. ^1H; 5.99, (d, J=13.5, 1H, CH=CHCl), 6.83, (d, J=13.5, 1H = CHCl), 3.13, (s, 1H, OH). ^{19}F; 1.12, (s, 6F).

Reaction of 2,2-Bis(trifluoromethyl)-3,4-difluoro-oxetane (4 and 5).

Anhydrous $AlCl_3$ (0.18m) and the oxetanes (0.122m) were heated at 80° for 6 hours. Distillation of the steam distilled reaction mixture gave a 35% yield of the cis -trans chlorofluoroxetanes(15,16). A small amount of(17) was isolated by glc.

Cis -2,2-Bis(trifluoromethyl)-3-fluoro-4-chlorooxetane (15). B.p. 43^0, (120 Torr). ir (gas) cm^{-1}: 1316, 1232, 982, (C-F), 730, 704, (CF$_3$). m/e 211 (M$^+$-Cl), 112. [(CF$_3$)$_2$ C=CHF]$^+$, 163 [CF$_2$ = C(CF$_3$)- CHF] $^+$. 80 (CHF = CHCl)$^+$, 69 (CF$_3$)$^+$. Calcd: C, 24.35; H, 0.82; Cl, 14.39. Fd: C, 24.20; H, 0.86; Cl, 14.03. ^{1}H; 5.52 (d,d, J=3.8, 52, 1H CHF), 6.46, (d,d, J=3.8, 10.8, 1H, CHCl). ^{19}F; -4.91 (d,q, J=8.7, 14.5, CF$_3$), -1.17 (d,q, J=8.7, 1.5, CF$_3$), 110.0 (d,d.q.q, J=52, 10.8, 1.5, 14.5, 1F).

Trans-2,2-Bis(trifluoromethyl)-3-fluoro-4-chlorooxetane (16). B.p. 69^0 (120 Torr). m/e (identical to the cis isomer) Fd: C, 24.46; H, 0.81; Cl, 14.18 ^{1}Hnmr 5.66 (d,d, J=4.5, 52 CHF) 6.54 (d,d, j=4.5, 8.0, CHCl).

1,1,1-Trifluoro-2-hydroxy-2-trifluoromethyl-3-fluoro-4,4-dichlorobutane (17). ir (gas) cm^{-1}: 3623, 3584, (O-H), 1333-1190. 1161. (C-F), 800 (C-Cl), 709, 699, (CF$_3$). m/e: 282 (M$^+$), 264 (M$^+$-H$_2$O), 246 (M$^+$-HCl), 227 (M$^+$-HCl-F), 182 [(CF$_3$)$_2$ C=CHF] $^+$, 69 (CF$_3$)$^+$. Calcd: C, 21.22; H, 1.07; Cl, 25.06. Fd: C, 21.12, H, 1.13, Cl, 25.01

^{1}H; 5.10 (d,d, J=4.0, 43.5, CHF), 6.08 (d,d, J=4.0, 14.0, CHCl$_2$), 3.68 (s,OH). ^{19}F; -29.28 (d,q, J=8.0, 10.0, 15.0, 10.0, 3F) -30.46 (d,q, J=15.0, 10.0, 3F), 91.41 (d,q,d,q, J=43.5m 15.0, 14.0. 8.0 1F).

When the cis isomer (4) was treated with AlCl$_3$ for 2 hours the yield of (15 and 16) was increased to 81%. The trans compound also gave (15) and (16) in 64% yield under mild conditions.

Reaction of 2,2-Bis(trifluoromethyl)-4,4-difluoro-oxetane (6).

The oxetane (0.114m) and AlCl$_3$ (0.34m) were heated at 70^0 for 8 hours. Distillation gave a 25% yield of the dichlorooxetane(18) and a 20% yield of the hydroxydichlorobutene (19).

2,2-Bis(trifluoromethyl)-4,4-dichlorooxetane (18). B.p. 80-83^0 (190 Torr.). ir (gas) cm^{-1}: 1324, 1230, C(C-F), 1087 (C-O-C), 1055, 962, (C-F),727, 690. m/e 227 (M$^+$-Cl), 207 (M$^+$-HCl-F), 193 (M$^+$-CF$_3$), 164, [(CF$_3$)$_2$ C=CH$_2$] $^+$, 96 (CCl$_2$ = CH$_2$)$^+$, 69 (CF$_3$)$^+$. Calcd: C, 22.93; H, 0.77. Fd: C, 22.68; H, 0.65. ^{1}H; 3.87 (s). ^{19}F; -2.31 (s).

1,1,1-Trifluoro-2-hydroxy-2-trifluoromethyl-4,4-dichloro-3-butene (19). B.p. 72-5^0 (90 Torr.). ir (gas) cm^{-1} 3597 (O-H), 3077 (=CH), 1621, (C=C), 1299 - 1212, 1183, 1157, 1018 (C-F), 962, 905, (C-Cl), 707, 662 (CF$_3$). m/e 262 (M+), 245 (M$^+$-OH), 193 (M$^+$-CF$_3$), 69 (CF$_3$)$^+$.

Calcd: C, 22.93; H, 0.77; Cl, 26.96. Fd: C, 22.60; H, 0.71; 27.05. ^{1}H; 3.84, (s, CH) 6.10 (s, OH). ^{19}F; -0.69 (s).

Reaction of 2,2-Bis(trifluoromethyl)-3,3-difluorooxetane (7).

The oxetane (0.1m) and $AlCl_3$ (0.2m) were heated at 70-80° for 6 hours. Distillation of the reaction mixture gave as sole product a 14.4% yield of 1,1,1-trifluoro-2-hydroxy-3,3-difluoro-4-chlorobutane (20A). B.p. 83° (137 Torr). Calcd: C, 22.53; H, 1.13. Fd: C, 22.52; H, 1.20. ^{1}H 3.74 (s, OH 4.01 (t,J=15.4). ^{19}F -0.15 (t, J=11.2, CF_3) 32.38 (t, Sept, J=11.2, 15.4).

Reaction of 2,2,3-Tris(trifluoromethyl)oxetane (8).

Distillation of the reaction mixture from [8], (0.06m) and $AlCl_3$ (0.09m) heated to 90 - 105° for 1.25 hours gave unreacted starting material and a 48% yield of 1,1,1-Trifluoro-2-hydroxy-2,3-bis(trifluoromethyl)-4-chlorobutane (20). B.p. 75° (100 Torr). ir(gas)cm^{-1}; 3636 (O-H), 1389 - 1053 (C-F), 993, 913 (C-Cl), 714, 698, 654. m/e 281 (M^+-OH), 259 (M^+-HF_2), 228 (M^+-HCF_3), 212 (M^+-HCl-CF_2), 193 (M^+-HCl-CF_3), 69 $(CF_3)^+$. Calcd: C, 24.14; H, 1.35. Fd: C, 24.12; H, 1.39. ^{1}H; 3.36 (q, J=7.5, 1H $CHCH_2Cl$), 3.55 - 4.33 (M, 2H), 3.72 (s,OH). ^{19}F -14.82 (m, 3F), -4.68 (m,6F).

Attempted Reaction of A Mixture of 2,2-Bis(trifluoromethyl-3,3,4-trifluorooxetane and the 3,4,4-trifluoro Isomer.

A mixture of the two oxetanes (0.2m) and aluminum chloride (0.25m) were heated in a stainless steel autoclave for 12 hours at 150°. Starting material and traces of a few other compounds were found.

Attempted Reaction of a Mixture of 2,2-Bis(trifluoromethyl)-3-fluorooxetane and the 4-fluoro Isomer with Potassium chloride.

The oxetanes (0.2m), KCl (0.2m), 18-crown- 6 ether (0.005m) and 25ml of acetonitrile were stirred vigorously for 17 hours. Care was taken to eliminate water from the starting materials and the reaction flask. Examination of the reaction mixture showed it to be starting oxetanes.

Reaction with Sulfuric Acid

2,2-Bis(trifluoromethyl)oxetane(1)

Sulfuric acid (5.1g) was added dropwise to the oxetane (0.05m) in a 3-necked flask held at 65-70° over a period of 20 minutes. Heating was continued for an additional hour. The mixture was cooled and the organic layer separated, washed with water, dried and distilled to give a 30% yield of the known 4,4,4-trifluoro-3-trifluoromethyl-1,3-butanediol (21), b.p. 75-79° (15 Torr.)[10].

Also bis(4,4,4-trifluoro-3-trifluoromethyl-3-hydroxybutyl) ether (22) was isolated in 12% yield. B.p. 90° (5 Torr.). ir (liquid), 3425 cm^{-1} (O-H), 2899 (C-H), 1342, 1204, 1149, 1086, 926, 758, 717.

m/e 406 (M^+), 389 (M^+-H_2O), 177 $[(CF_3)_2CH-CH_2]^+$,69 $(CF_3)^+$. Calcd: C, 29.57; H, 2.48. Fd: C, 29.36; H, 2.40. ^1H; 4.35 (s,OH), 2.25 (t, J=6.0, CH_2), 3.82 (t, J=6.0, CH_2O).

2,2-Bis(trifluoromethyl)-4-fluorooxetane(2)

From essentially the procedure above, a considerable portion of oxetane was recovered together with three other compounds. The unsaturated aldehyde, 1,1,1-trifluoro-2-trifluoromethyl-2-butenal (23), was obtained in 13% yield. ^1H; and ^{19}F nmr and ir spectra were identical to the known compound [9].

There also was obtained a dioxene, 2-(3,3,3-trifluoro-2-trifluoromethyl-1-propenyl)-4,4-bis(trifluoromethyl)-1,3-diox-5-ene (24) in 22% yield. B.p. 47-51° (15 Torr.), ir (liq) cm^{-1} 1667 (C=C), m/e 384 (M^+), 365 (M^+-F), 315 (M^+-CF_3), 191 $[(CF_3)_2C{=}CHO]^+$, 173 $[CF_2C(CF_3){=}CHCHO]^+$, 69 $(CF_3)^+$. Calcd: C, 31.27; H, 1.05; Found: C, 3104; H, 0.93. ^1H; 7.06, 5.28, 6.03, 5.72, (all d, all J=6.0). ^{19}F -18.74 (q, J=7.2, $=CCF_3$), -12.73 (q, J =7.2, $=CCF_3$). -2.71 (q, J= 10.5, CF_3-C) -1.19 (q, J= 10.5, C-CF_3).

A dioxetane, 2-(3,3,3-trifluoro-2-trifluoromethyl-1-propenyl)-4-(3,3,3-trifluoro-2-trifluoromethyl-2-hydroxy propyl)-1,3-dioxetane[25], was isolated in 24% yield. B.p. 87-90°(1 Torr.) ir (liquid), cm^{-1}, 3559 (O-H), 1661 (C=C), 1333 -1136, 1081, 971, 752, 714. m/e 402 (M^+), 382 (M^+-F), 333 (M^+-CF_3), 191 $[(CF_3)_2C{=}CHCO]^+$, 209 $[(CF_3)_2C(OH)CH_2CO]^+$, 69 $(CF_3)^+$ Calcd: C, 29.87; H, 1.50. Found: 29.69; H, 1.41. ^1H; 3.93 (s, OH), 6:98 (d, J = 6.0, HC=), 5.20 (d, J=6.0, C=C-CH), 5.51 (t,J=5.5 CH_2CHO_2) 2.51 (d, J=5.5 2H). ^{19}F -0.92, -2.59, -0.34, -0.94 (all q, all J= 10.0).

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