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HETEROCYCLIC POLYFLUORO-COMPOUNDS. PART 36 [1]. THE REACTION OF 2,2-BIS(TRIFLUOROMETHYL)-3,4-DIFLUORO-OXETAN WITH ALUMINIUM TRICHLORIDE

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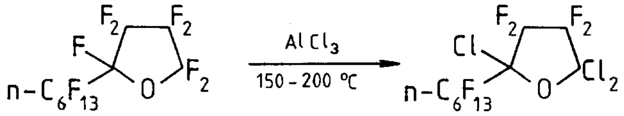
SUMMARY

2,2-Bis(trifluoromethyl)-3,4-difluoro-oxetan, when treated with aluminium trichloride at 30 to 90 °C, undergoes cis to trans isomerisation, non-stereospecific exchange of the 4-fluorine by chlorine, and more slowly of the 3-fluorine, and ring opening to give preferentially the alcohols $(CF_3)_2C(OH)CX{=}CHCl$ (X = F or Cl), together with the aldehydes $(CF_3)_2CClCHXCHO$ and acid chlorides $(CF_3)_2CClCHXCClO$ (X = F or Cl). A large number of unidentified minor products were also obtained from the reactions carried out at the higher temperatures.

INTRODUCTION

Perfluoroethers are chemically robust and inert to most reagents; one of the few reactions they show is the exchange of fluorines adjacent to the oxygen when they are treated with aluminium trichloride [2,3], *e.g.*,



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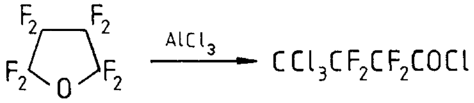
The reaction may be accompanied by C–O bond cleavage, when α-perfluoroalkyl groups are absent [3,4], *e.g.*,



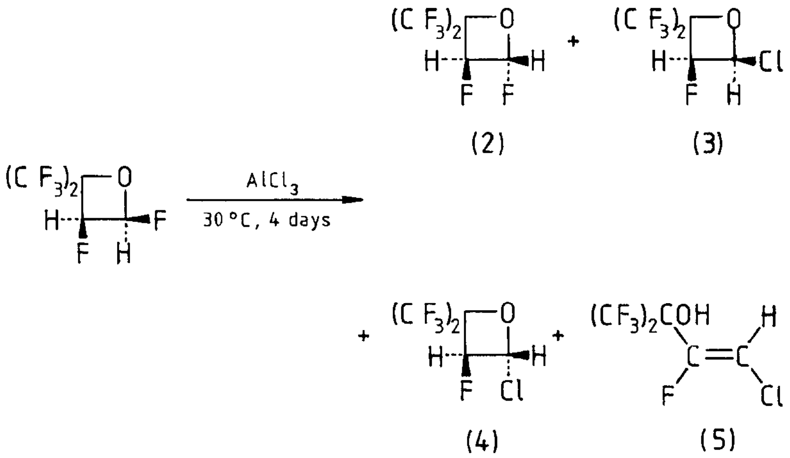
Partially fluorinated ethers undergo exchange under milder conditions [5]:

$$(CHF_2CHF)_2O \xrightarrow[100\text{–}120\ ^{o}C]{AlCl_3} CHF_2CHClOCHFCHF_2 + (CHF_2CHCl)_2O$$

RESULTS

Mixtures of *cis*- and *trans*-2,2-bis(trifluoromethyl)-3,4-difluoro-oxetan are obtained from the photochemical addition of hexafluoroacetone to (*Z*)- or (*E*)-1,2-difluoroethylene [6], and the individual isomers, obtainable by g.l.c. separation, offer advantages for the study of this type of reaction. They have two types of ring fluorine, only one of which is adjacent to oxygen and hence expected to be more readily exchanged, and the geometry of any exchange should be amenable to characterisation. We here describe the results of a study of their heterogeneous reactions with *ca.* one equivalent of aluminium trichloride under milder conditions than those found necessary for the exchange of fully fluorinated ethers. At moderate temperatures (30-42 °C), *cis* to *trans* isomerisation and exchange of the fluorine adjacent to oxygen predominated, but at a somewhat higher temperature (86 °C) the reaction was much more complex, particularly when the *trans*-difluoro-oxetan was used, and the multitude of minor products could not be completely characterised.

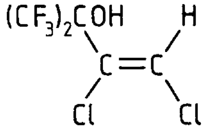
The cis-isomer (1), when treated with aluminium trichloride at 30 °C for 4 days, underwent 83% conversion, and gave the *trans*-isomer (2) (36%), together with the *cis*- (7%) and *trans*-



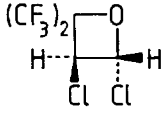
Scheme 1

chloro-oxetans (38%), (3) and (4), and the ring-opened product, allyl alcohol (5) (2%) (Scheme 1).

The *trans*-isomer underwent slower exchange, and was converted into equimolar amounts of the chloro-oxetans (3) and (4) to the extent of 24% in 3 days at 42 °C. At 86 °C during 3 h, the *cis*-oxetan (1) underwent complete conversion, giving the compounds (2) (30%), (3) (22%), (4) (40%), and (5) (3%), and a trace of the dichloro-substituted allyl alcohol (6). Under similar conditions, the *trans*-oxetan (2) gave a very



(6)



(7)

complex product mixture, which contained the compounds (4) (8%), (5) (16%), (6) (38%), and the *trans*-dichloro-oxetan (7) (5%), as major components, together with at least 15 other components.

Some of these could be identified with reasonable certainty by mass spectrometry, and included the aldehydes (8) [X = F (3%) or Cl (4%)], the related acid chlorides (9) [X = F (1%) or Cl (5%)], trace amounts of the (*E*)-isomers of alcohols (5) and (6), and the *cis*-isomer of (7) (0.3%).

$(CF_3)_2CClCHXCHO$
(8)

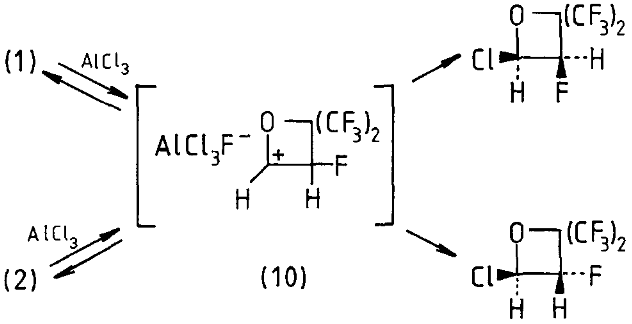
$(CF_3)_2CClCHXCOCl$
(9)

The individual *cis*- and *trans*-4-chloro-oxetans, (3) and (4), were also studied, in an attempt to trace the reactions subsequent to exchange of the fluorine adjacent to oxygen. Brief reaction times were used in an attempt to minimise complications, but the temperature selected was, of necessity, higher than that used for exchange of one fluorine in the difluoro-oxetans.

At 75 °C during 5 min, the *cis*-oxetan (3) underwent 69% conversion, and gave the *trans*-oxetan (4) (3%), the *trans*-dichloro-oxetan (7) (44%), and the alcohol (6) (16%). Under similar conditions, the *trans*-oxetan (4), conveniently obtained from the reaction of a mixture of difluoro-oxetans (1) and (2) with aluminium trichloride at 90 °C during 5.5 h, underwent 69% conversion also, and gave the alcohols (5) (5%) and (6) (34%), and dichloro-oxetan (7) (18%).

The following observations need to be accounted for: (i) isomerisation of a *cis*-oxetan to its *trans*-isomer may occur without introduction of chlorine; (ii) replacement of fluorine by chlorine occurs more readily for the fluorine adjacent to oxygen but it is not stereospecific, and the *cis*-oxetans appear to be more reactive; and (iii) ring opening occurs by C-O bond cleavage, with the O-CHCl bond broken preferentially. Tiers [2] proposed a carbenium ion mechanism for the exchange, which for oxetans (1) and (2) would be of the type shown in Scheme 2.

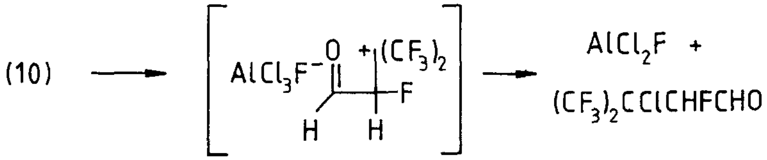
If formation of the carbenium ion intermediate (10) is reversible, the isomerisation is accounted for. The absence of *trans* to *cis* isomerisation is presumably then a consequence of the greater thermodynamic stability of the *trans*-isomer.



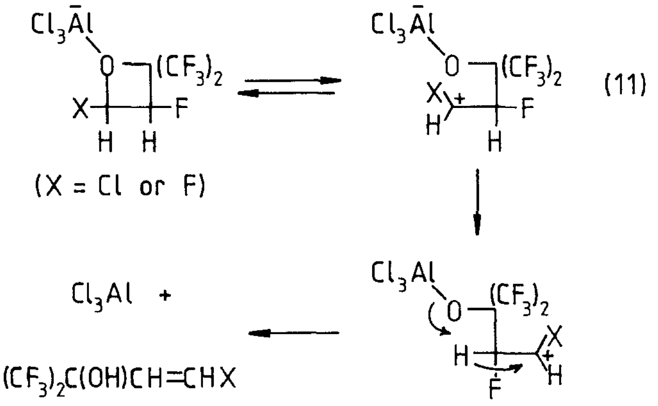
Scheme 2

The more reluctant exchange of the second fluorine is understandable, since the necessary carbenium ion is no longer stabilised by an adjacent oxygen. Recently, Tatlow and his co-workers have observed an enantiomeric isomerisation analogous to ours in acyclic polyfluoro-ethers [5].

As for ring-cleavage reactions, β-cleavage of (10) would account for the formation of the less favoured aldehyde product:



and the acid chloride may possibly arise by its subsequent chlorination, but this does not account for the allyl alcohols (5) and (6). An alternative possibility is shown in Scheme 3, and this would account for both isomerisation, since the open-chain intermediate (11) can undergo bond rotation followed by recyclisation, and allyl alcohol formation. Cleavage of the other C–O bond, required for the formation of (8) and (9), leaves a cationic centre unstabilised by the substituent X (F or Cl). A CF_3 group should show no stabilisation. It is possible to incorporate halogen exchange into this scheme, by



Scheme 3

incorporating a step involving addition of Cl^- to (11) (X = F) and removal of F^-. However, exchange of the fluorine at the 3-carbon still requires its direct removal by aluminium trichloride in either a two-step process involving carbenium ion formation, or in a one-step process involving exchange in a cyclic transition state, when non-stereospecificity remains to be accounted for.

EXPERIMENTAL

Techniques used were similar to those previously described [6]. 2,2-Bistrifluoromethyl-3,4-difluoro-oxetan was prepared by the photochemical addition of hexafluoroacetone to 1,2-difluoroethylene [6]. All aluminium trichloride was freshly sublimed

The technique of g.l.c. coupled mass spectrometry proved invaluable in the monitoring of complex product mixtures, and providing evidence for the structures of minor components. When individual components were not separated, the quoted yields were estimated using g.l.c. (assuming equal detector responses for the various components), combined, where possible, with data obtained from g.l.c.-coupled mass spectrometry, and n.m.r. spectroscopy.

The Reaction of 2,2-Bis(trifluoromethyl)-3,4-difluoro-oxetan with Aluminium Trichloride

(*a*) cis/trans-Isomers at 90 °C

A 1.0:2.7 mixture of the *cis*- and *trans*-oxetans (3.108 g, 13.48 mmol) and aluminium trichloride (2.651 g, 19.86 mmol), sealed in a Pyrex ampoule (50 cm^3) *in vacuo* and shaken at 90 °C for 5.5 h, gave after fractionation by trap-to-trap distillation *in vacuo*, an unidentified mixture (0.58 mmol) of four (by g.l.c.) components which condensed at -130 °C, and a liquid fraction (3.315 g), condensing at -25 and -45 °C, from which were separated by g.l.c. (4 m Kel-F No. 10 oil on Celite at 60 °C) the major components *trans*-2,2-bis(trifluoromethyl)-4-chloro-3-fluoro-oxetan (nc) (4) (1.367 g, 5.55 mmol, 41% yield) (Found: C, 24.4; H, 1.1; F, 53.9. $C_5H_2ClF_7O$ requires C, 24.3; H, 0.8; F, 54.0%) and an inseparable 2.6:1.0 mixture (1.047 g) comprising (by n.m.r.) *cis*-2,2-bis(trifluoromethyl)-4-chloro-3-fluoro-oxetan (3) and (*Z*)-4-chloro-1,1,1,3-tetrafluoro-2-trifluoromethylbut-3-en-2-ol (5). The minor components (0.901 g) remained unidentified.

(*b*) cis-Oxetan at 30 °C

The *cis*-oxetan (0.593 g, 2.58 mmol) and aluminium trichloride (0.473 g, 3.55 mmol), after shaking at 30 °C for 4 days, gave a mixture which was removed (0.613 g) and shown by n.m.r. spectroscopy, mass spectrometry, and g.l.c. (4 m Kel-F No. 10 oil on Celite at 79 °C) to comprise recovered *cis*-oxetan (0.103 g, 0.45 mmol, 17%), *trans*-2,2-bis(trifluoromethyl)-3,4-difluoro-oxetan (2) (0.214 g, 0.93 mmol, 36%), *cis*-2,2-bis(trifluoromethyl)-4-chloro-3-fluoro-oxetan (3) (42 mg, 0.17 mmol, 7%), *trans*-2,2-bis(trifluoromethyl)-4-chloro-3-fluoro-oxetan(4) (0.239 g, 0.97 mmol, 38%), and (*Z*)-4-chloro-1,1,1,3-tetrafluoro-2-trifluoromethylbut-3-en-2-ol (5) (15 mg, 0.06 mmol, 2%).

(*c*) cis-Oxetan at 86 °C

The *cis*-oxetan (1.187 g, 5.16 mmol) and aluminium trichloride (0.983 g, 7.36 mmol), similarly shaken at 86 °C for 3 h, gave a volatile mixture (1.980 g) which was separated by g.l.c. (2 m MS 550 silicone oil on Chromosorb at 86 °C) to give *trans*-

2,2-bis(trifluoromethyl)-3,4-difluoro-oxetan (0.357 g, 1.55 mmol, 30%), *trans*-2,2-bis(trifluoromethyl)-4-chloro-3-fluoro-oxetan (4) (0.851 g, 2.08 mmol, 40%), and *cis*-2,2-bis(trifluoromethyl)-4-chloro-3-fluoro-oxetan (nc) (3) (0.649 g, 1.13 mmol, 22%) (Found: C, 24.1; H, 0.7; F, 54.1. $C_5H_2ClF_7O$ requires C, 24.3; H, 0.8; F, 53.9%). Two minor components were identified by mass spectrometry as (*Z*)-4-chloro-1,1,1,3-tetrafluoro-2-trifluoromethylbut-3-en-2-ol (5) (37 mg, 0.15 mmol, 3%) and (*Z*)-3,4-dichloro-1,1,1-trifluoro-2-trifluoromethylbut-3-en-2-ol (6) (<1%).

(*d*) trans-*Oxetan at 42 °C*

The *trans*-oxetan (0.817 g, 3.55 mmol) and aluminium trichloride (0.734 g, 5.51 mmol), similarly shaken at 42 °C for 3 days, gave a volatile product (0.830 g) which was shown by n.m.r. spectroscopy, mass spectrometry, and g.l.c. (4 m Kel-F No. 10 oil on Celite at 77 °C) to comprise the *trans*-difluoro-oxetan (0.638 g, 2.73 mmol, 77%), the *cis*-4-chloro-3-fluoro-oxetan (3) (0.101 g, 0.41 mmol, 12%) and the *trans*-4-chloro-3-fluoro-Oxetan (4) (0.101 g, 0.41 mmol, 12%).

(*e*) trans-*Oxetan at 86 °C*

The *trans*-oxetan (1.200 g, 6.86 mmol) and aluminium trichloride (0.913 g, 6.86 mmol), similarly shaken at 86 °C for 3 h, gave a volatile product (1.423 g) from which were separated by g.l.c. (2 m MS 550 silicone oil on Celite at 90 °C) the major components *trans*-2,2-bis(trifluoromethyl)-4-chloro-3-fluoro-oxetan (4) (0.101 g, 0.41 mmol, 8%), *trans*-2,2-bis(trifluoromethyl)-3,4-dichloro-oxetan (nc) (7) (68 mg, 0.26 mmol, 5%) (Found: 22.6; H, 0.7; F, 43.1. $C_5H_2Cl_2F_6O$ requires C, 22.8; H, 0.8; F, 43.3%), (*Z*)-4-chloro-1,1,1,3-tetrafluoro-2-trifluoromethylbut-3-en-2-ol (nc) (5) (0.205 g, 0.83 mmol, 16%) (Found: C, 24.1; H, 0.8; F, 54.1. $C_5H_2ClF_7O$ requires C, 24.3; H, 0.8; F, 53.9%), and (*Z*)-3,4-dichloro-1,1,1-trifluoro-2-trifluoromethylbut-3-en-2-ol (nc) (6) (0.518 g, 1.97 mmol, 38%) (Found: C, 22.9; H, 0.8; F, 43.6. $C_5H_2Cl_2F_6O$ requires C, 22.8; H, 0.8; F, 43.3%). At least 15 minor components remained, and g.l.c. coupled mass spectrometry indicated the presence of

3-chloro-2,4,4,4-tetrafluoro-3-trifluoromethylbutanoyl chloride (9, X = F) (11 mg, 0.04 mmol, 1%), 2,3-dichloro-4,4,4-trifluoro-3-trifluoromethylbutanoyl chloride (9, X = Cl) (77 mg, 0.26 mmol, 5%), 3-chloro-2,4,4,4-tetrafluoro-3-trifluoromethylbutanal (8, X = F) (37 mg, 0.15 mmol, 3%), 2,3-dichloro-4,4,4-trifluoro-3-trifluoromethylbutanal (8, X = Cl) (55 mg, 0.21 mmol, 4%), (*E*)-4-chloro-1,1,1,3-tetrafluoro-2-trifluoromethylbut-3-en-2-ol (2 mg, 0.01 mmol), (*E*)-3,4-dichloro-1,1,1-trifluoro-2-trifluoromethylbut-3-en-2-ol (3 mg, 0.01 mmol), recovered *trans*-oxetan (9 mg, 0.04 mmol), and *cis*-2,2-bis(trifluoromethyl)-3,4-dichloro-oxetan (3 mg, 0.01 mmol), with unidentified material.

The Reaction of 2,2-Bis(trifluoromethyl)-4-chloro-3-fluoro-oxetan with Aluminium Trichloride at 75 °C

(*a*) trans-*Isomer*

The *trans*-oxetan (1.255 g, 5.09 mmol) and aluminium trichloride (0.815 g, 6.13 mmol), shaken at 75 °C for 5 min, gave a volatile mixture shown by mass spectrometry, n.m.r. spectroscopy, and g.l.c. to comprise recovered *trans*-oxetan (0.389 g, 1.58 mmol, 31%), (*Z*)-3,4-dichloro-1,1,1-trifluoro-2-trifluoromethylbut-3-en-2-ol (0.455 g, 1.73 mmol, 34%), *trans*-2,2-bis(trifluoromethyl)-3,4-dichloro-oxetan (0.241 g, 0.91 mmol, 18%), and (*Z*)-4-chloro-1,1,1,3-tetrafluoro-2-trifluoromethylbut-3-en-2-ol (60 mg, 0.25 mmol, 5%), together with unidentified material (0.171 g).

(*b*) cis-*Isomer*

The *cis*-oxetan (1.228 g, 4.98 mmol) and aluminium trichloride (0.800 g, 6.00 mmol), shaken at 75 °C for 5 min, gave a product similarly shown to comprise recovered *cis*-oxetan (0.380 g, 1.54 mmol, 31%), the *trans*-4-chloro-3-fluoro-oxetan (37 mg, 0.15 mmol, 3%), *trans*-2,2-bis(trifluoromethyl)-3,4-dichloro-oxetan (0.576 g, 2.19 mmol, 44%), and (*Z*)-3,4-dichloro-1,1,1-trifluoro-2-trifluoromethylbut-3-en-2-ol (0.210 g, 0.80 mmol, 16%), together with unidentified material (84 mg).

The Structure of the Products

It proved impossible to isolated pure samples for analysis and characterisation of all the minor components produced in these reactions for a number of reasons. In particular, g.l.c. separation from the very complex product mixture was very difficult, and on the reaction scale possible with the limited quantities of starting material available, only mg quantities were produced.

(*a*) 2,2-Bis(trifluoromethyl)-4-chloro-3-fluoro-oxetan

Both isomers had i.r. spectra which indicated the absence of unsaturation. The isomer with the shorter g.l.c. retention time was assigned the *trans*-configuration on the following grounds. It show δ_F (positive values to low field of external CF_3CO_2H) 3.0 [CF_3 *cis* to F, ^4J (CF_3,CF_3) = 9, ^4J (CF_3,F) = 15 Hz], -0.9 [CF_3, ^4J (CF_3,F) = 2 Hz], and -112.3 p.p.m. [CF, ^2J (H,F) = 52, ^3J (H,F) = 11 Hz], and δ_H ($SiMe_4$) 5.20 [CCHC, ^3J (H,H) = 4 Hz] and 6.13 p.p.m. (CHO), while the *cis*-isomer showed δ_F 4.2 [CF_3 *cis* to F, ^4J (CF_3,CF_3) = 9, ^4J (CF_3,F) = 15 Hz], -1.5 [CF_3, ^4J (CF_3,F) = 2 Hz], and -122.1 p.p.m. [CF, ^2J (H,F) = 52, ^3J (H,F) = 7.5 Hz], and δ_H 5.42 [CCHC, ^3J (H,H) = 5 Hz] and 6.28 (CHO). The absence of a low-field absorption for a ring fluorine shows that the chlorine is introduced next to oxygen, and this is confirmed by the magnitude of ^2J (H,F) which shows that the CHF group is attached to carbon rather than oxygen where larger magnitudes are observed [6]. The starting difluoro-oxetans show fluorine absorptions for this CHF group at -122.6 p.p.m. for the *trans*-isomer and -133.7 for the *cis*-isomer. Introduction of chlorine results in the expected low-field shift, which, somewhat unexpectedly, is only marginally greater when chlorine is *cis* to fluorine rather than *trans*. However, the magnitudes of ^3J (H,H) [6] and ^3J (H,F) [6], where J_{cis} is greater than J_{trans} leave no doubt about the assignment.

The mass spectra of the isomers were very similar, differing only in the relative intensities of the ions, and prominent ions (>50%) included m/e 211 ($C_5H_2F_7O$), 182 (C_4HF_7, 100%), 163 (C_4HF_6), 113 (C_3HF_4), 69 (CF_3), 45 (C_2H_2F), and 29 (CHO). The $C_4HF_7^{+\cdot}$ ion in particular is strong evidence for the 3-fluorine substituent.

(b) 2,2-Bis(trifluoromethyl)-3,4-dichloro-oxetan

Here, only one isomer was isolated in sufficient amounts for characterisation, but a component of longer retention time showed a very similar mass spectrum. The isomer isolated showed δ_F 3.5 and -0.7 p.p.m. (CF_3) and δ_H 4.92 [CCHC, ^3J (H,H) = 5.5 Hz] and 6.09 p.p.m. (CHO). It is assigned the trans-configuration large on the grounds of the magnitude of the trans-H,H-coupling constant. In the corresponding difluoro-oxetan, this coupling constant has a magnitude of 2.5 Hz [6], replacement of one fluorine by chlorine results in a rise to 4 Hz, resulting in a predicted 5.5 Hz in the dichloro-compound. In the cis-difluoro-oxetan, the H,H-coupling constant has a magnitude of 3.5 Hz, this rises to 5 Hz in the chloro-oxetan, leading to a predicted 6.5 Hz in the cis-dichloro-oxetan, significantly larger than observed. The g.l.c. retention time is in accord with this assignment, in that the more polar cis-isomer is eluted last.

The mass spectrum of each of the two isomers has a base peak corresponding to the $C_4H^{35}ClF_6^{+\cdot}$ ion and prominent ions (>10%, only ^{35}Cl containing ions reported) corresponding to m/e 227 ($C_5H_2ClF_6O$), 163 (C_4HF_6), 129 (C_3HClF_3), 113 (C_3HF_4), 96 ($C_2H_2Cl_2$), 85 ($CClF_2$), 75 (C_3HF_2), 69 (CF_3), 61 (C_2H_2Cl) and 51 (CHF_2).

(c) 4-Chloro-1,1,1,3-tetrafluoro-2-trifluoromethylbut-3-en-2-ol

Only one isomer was isolated; this was assigned the (Z)-configuration, but a further component, detected in trace amounts, showed a very similar mass spectrum and thus should be the (E)-isomer. The major isomer showed $\nu_{max.}$ ca. 3450 br and 3650 sh cm^{-1} (OH str.) and δ_F 0.5 [CF_3, ^4J (F,F) = 8 Hz] and -44.0 p.p.m. [CF, ^3J (H,F) = 22 Hz], and δ_H 3.7 (OH, br., exchanging with D_2O) and 6.12 p.p.m. (CH). The magnitude of the H,F-coupling constant is characteristic of trans-nuclei [7].

The mass spectrum of each of the isomers showed a molecular ion, and prominent ions (>10%, only ^{35}Cl containing ions are reported) with m/e 177 ($C_4H_2ClF_4O$), 157 (C_4HClF_3O), 107 (C_3HClFO,100%), 79 (C_2HClF), and 68 (CF_3). There was a notable resemblance to the mass spectra of similar allylic alcohols [8].

(d) 3,4-Dichloro-1,1,1-trifluoro-2-trifluoromethylbut-3-en-2-ol

The compound isolated was assigned the (Z)-configuration largely by analogy with the previous compound, and again a compound, presumed to be the (E)-isomer, was detected by mass spectrometry, but was not isolated. The major isomer showed $\nu_{max.}$ 3570 cm^{-1} (OH str.), δ_F 1.8 p.p.m. (CF_3), and δ_H 3.68 (OH, exchanging with D_2O) and 6.88 p.p.m. (=CH). The mass spectrum, and that of its supposed isomer, showed a molecular ion, and prominent ions (>10%, only ^{35}Cl containing ions are reported) with m/e 198 (C_4HClF_6), 193 ($C_4H_2Cl_2F_3O$), 173 ($C_4HCl_2F_2O$), 163 (C_4HF_6), 123 (C_3HCl_2O), 95 (C_2HCl_2), 85 (C_4H_2FO), 83 (C_4FO), 75 (C_3HF_2), 69 (CF_3), 61 (C_2H_2Cl), 60 (C_2HCl), and 53 (C_3HO).

(e) 3-Chloro-2,4,4,4-tetrafluoro-3-trifluoromethyl-butanoyl chloride

The identity of this component rests solely on mass spectrometric grounds. It showed ions (only ^{35}Cl containing reported) with m/e 245 (C_5HClF_7O, 44.5), 182 (C_4HF_7, 67.5), 163 (C_4HF_6, 14.0), 147 (C_3F_5O, 10.5), 113 (C_3HF_4, 38.9), 97 (C_2F_3O, 24.6), 85 ($CClF_2$, 12.9), 79 (C_2HClF, 11.9), 69 (CF_3, 100.0), 63 ($CClO$,59.8), 51 (CHF_2, 17.6), and 44 (C_2HF, 41.5). The very prominent $COCl^+$ is very characteristic of an acid chloride, and ions corresponding to $(CF_3)_2CClCHF\overset{+}{C}O$, $(CF_3)_2CCHF^{+\bullet}$, $(CF_3)_2CCH^+$, CF_3CCHF^+, and $CHFCCl^+$ delineated the carbon skeleton.

(*f*) 2,3-Dichloro-4,4,4-trifluoro-3-trifluoromethylbutanoyl chloride

This compound too rests upon mass spectrometric evidence. It showed ions (only ^{35}Cl containing reported) with *m/e* 261 ($C_5HCl_2F_6O$, 30.0), 198 (C_4HClF_6, 91.5), 163 (C_4HF_6, 54.9), 129 (C_3HClF_3, 11.2), 95 (C_2HCl_2, 15.0), 85 ($CClF_2$, 24.2), 75 (C_3HF_2, 13.5), 69 (CF_3, 100.0), 63 (CClO, 21.3) 44 (C_2HF, 43.2), and 36 (HCl, 12.1%). It resembled the previous example in its fragmentation, with chlorine replacing fluorine in the appropiate ions: $(CF_3)_2CClCHClCO^+$, $(CF_3)_2CCHCl^{+\bullet}$, CF_3CCHCl^+, and $CHClCCl^+$.

A mixture containing these two acid chlorides showed $\nu_{max.}$ 1802 and 1786 cm^{-1} (C=O str.).

(*g*) 3-Chloro-2,4,4,4-tetrafluoro-3-trifluoromethylbutanal

This too rests upon mass spectrometric evidence. It showed ions (only ^{35}Cl containing reported) with *m/e* 246 ($C_5H_2ClF_7O$, *M*, 1.4), 245 (C_5HClF_7O, 11.1), 216 (C_4ClF_7, 74.5), 182 (C_4HF_7, 15.7), 181 (C_4F_7, 57.7), 147 (C_3F_5O, 27.1), 113 (C_3HF_4, 11.7), 97 (C_2F_3O, 27.0), 85 (C_4H_2FO, 37.9), 83 ($C_2H_2F_3$, 44.8), 79 (C_2HClF, 15.4), 69 (CF_3, 100.0), 44 (C_2HF, 48.5), and 29 (CHO, 32.1%). The $(M - H)^+$ and CHO^+ ions indicate strongly the presence of an aldehyde function, and apart from these, it shows the expected resemblance to the acid chloride of (*e*) above.

(*h*) 2,3-Dichloro-4,4,4-trifluoro-3-trifluoromethylbutanal

Again, mass spectrometry provides the sole evidence for this minor compound, showing ions (only ^{35}Cl containing reported) with *m/e* 262 ($C_5H_2Cl_2F_6O$, *M*, 1.2), 261 ($C_5HCl_2F_6O$, 30.0), 198 (C_4HClF_6, 91.5), 163 (C_4HF_6, 54.9), 129 (C_3HClF_3, 11.2), 95 (C_2HCl_2, 15.0), 69 (CF_3, 100.0), 67 (C_2H_2ClO, 10.4), 60 (C_2HCl, 37.6), 36 (HCl, 12.1), and 29 (CHO, 21.3). The features common to the acid chlorides of (*f*) and aldehyde of (*g*) indicate its structure.

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