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Chloropolyfluoro-derivatives of ethyl methyl ether

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Abstract

Fluorination of 2-chloroethyl methyl ether by potassium tetrafluorocobaltate at 180–250 °C gave various tri-, tetra-, penta- and hexafluoro(2-chloroethyl methyl) ethers. Cobalt trifluoride afforded the same products in poorer recoveries. Structures were established spectroscopically. Cl_2–UV and $CHClFCHFOCHF_2$ gave halogeno-ethers by exchange of Cl for both H and also F. © 1997 Elsevier Science S.A. All rights reserved.

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1. Introduction

Oxygen-containing organic compounds, which have been fluorinated by high valency transition metal fluorides in this Department [1], have included diethyl ether and ethyl methyl ether, as reported earlier [2]. Ether linkages were preserved and the polyfluoro-diethyl and -ethyl methyl ethers, respectively obtained, mostly had an ethyl group converted to 1,2,2-trifluoroethyl. This function was quite stable and dehydrofluorination to the difluorovinyl unit was difficult [2,3]. Loss of HF is inhibited by the adjacent oxygen as for polyfluorides with heterocyclic rings, and occurs much less readily than from many polyfluorocycloalkanes, for example [1].

The work was extended shortly afterwards to chlorine-containing ethers, and products from fluorinations of 2-chlorodiethyl ether and 2-chloro-2,2-difluoroethyl ethyl ether by cobalt trifluoride have been reported recently [4]. A further aspect of the work is now described, covering the fluorination of 2-chloroethyl methyl ether. Cobalt trifluoride gave unsatisfactory results with this ether, and so potassium tetrafluorocobaltate, a milder reagent [1], was used.

2. Results and discussion

2-Chloroethyl methyl ether (**I**) was passed over a stirred bed of potassium tetrafluorocobaltate contained in a standard metal reactor held at temperatures between 180 and 250 °C. The mixture of products was separated by gas chromatography. As for the other ethers (cf. [2,4]), fluorination occurred without extensive rupture of the ether linkage, and there was little elimination of chlorine. The major products (**II–XI**) were polyfluorinated 2-chloroethyl methyl ethers, the structures and detailed characteristics of the individual compounds isolated being recorded in Section 3.2.

Fluorination of **I** using cobalt trifluoride gave much poorer recoveries of chlorofluoro-ethers (**V–XI** were isolated) even at temperatures of 75–90 °C.

All of the products obtained had fluoro- or difluoro-methyl groups and included four known ethers with $-OCF_2-$ moieties in the ethyl groups. As before [4], structures were established by NMR and mass spectrometry. New ethers found had $-CHFCClF_2$ units (**V** and **VI**), or $-CHFCHClF$ units (**VIII–XI**).

All the peaks present in the ^{19}F and ^1H NMR spectra of these products were related to specific functions, characteristic signal forms and coupling constants (of around 50–70 Hz) for $>CHF$, $-CHF_2$, $-CH_2F$, and $-CHClF$ groups being of special importance. Significant peaks present in the mass spectra of the products arose from fragments that corresponded with the structures deduced from the NMR evidence.

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The chloropolyfluoro ethyl methyl ethers, **II**–**XI**, were thus characterized completely.

Each of formula **IV**–**VI** has one chiral centre, and the compounds isolated were enantiomeric pairs. Compounds **VIII** and **IX** ($CHClFCHFOCHF_2$) were a diastereoisomeric pair (erythro- and threo-forms, each with two enantiomers), the structure having two chiral centres. Which compound had which form was not established. Compounds **X** and **XI** were analogous, but with $-CH_2F$ groups.

Attempts were made to dehydrohalogenate a mixture of diastereoisomers **VIII** and **IX**. Using aqueous potassium hydroxide (20 M), starting material was recovered. Fused KOH at 160 °C afforded some starting material containing ca. 20% of unidentifiable shorter retained (GLC) components. The only reagent to give any recognizable product was powdered KOH in refluxing benzene (cf. [5]). Even so, recoveries were poor and the product mixture was not separated. The major constituent was shown by NMR spectroscopy to be (*Z*)-difluoromethyl 1,2-difluorovinyl ether, and its (*E*)-stereoisomer was also present. Other minor vinylic species were also detected, probably chlorine containing. As with other oxygenated species [1], removal of HF under basic conditions is very difficult. In this case, the same applies to HCl.

Chlorination of a mixture of **VIII** and **IX** in a sealed hard glass tube irradiated by UV light gave, as the major product, $CCl_2FCClFOCHF_2$ (**XII**), accompanied by $CCl_2FCClFOCClF_2$ (**XIII**). Traces of $C_2Cl_5OCHF_2$ (**XIV**) and of C_2Cl_6 (**XV**) were also found: all were isolated and characterized. Several minor products (**XVI**–**XX**) had higher proportions of chlorine than **XII** and **XIII**, but could not be purified or identified with absolute certainty (see Section 3.4). The hydrogens in the chlorodifluoroethyl group are obviously replaced more readily than that in difluoromethyl. Complete halogenation of the methyl group is difficult (no trifluoromethyl ethers were detected among the products of the original fluorination).

Much more surprising in this reaction, however, is that chlorine can displace fluorine from the polychloro-ether products, such as **XII** and **XIII**, under relatively mild free-radical conditions, and despite the greater steric demands of chlorine as a substituent. Though **XIV** and **XV** were the only products of this type to be isolated, there is no doubt that others were present, and tentative structures (**XVI**–**XX**) have been postulated (Section 3.4). Presumably, the expelled fluorine reacted ultimately with the glass walls of the reaction tube.

There is an earlier example of an exchange of this type [3]. Chlorination of 1,2,2-trifluoroethyl methyl ether gave a mixture of 1,2,2-trifluoroethyl chloromethyl ether and 1-chloro-2,2-difluoroethyl methyl ether.

Conversions of C–F bonds in aliphatic fluorides to C–Cl have long been known [6], but the chlorinating species are usually Lewis acid-type reagents such as aluminium chloride. Most examples have involved C–F bonds adjacent to ether-oxygen [7], or to C=C bonds [6]. Some such exchanges were effected on polyfluorodiethyl ethers [3]. Replacement of F by Cl following orthodox reactions with elemental chlorine under UV irradiation, but in the absence of an ionic catalyst, is not normally encountered however.

3. Experimental details

3.1. General

Gas-liquid chromatography. Small-scale preparative GLC separations were carried out in Pye 104 or 105 machines, using 9.1 m × 7 mm tubes having the following packings: A, polyethyleneglycol adipate:Chromosorb P30-60 (1:4); B, dinonyl phthalate:Celite (1:2); C, silicone gum:Supasorb (1:19). For each separation, the unit used, temperature (°C), and nitrogen carrier gas flow rate ($l\ h^{-1}$) are given.

Spectroscopy. Nuclear magnetic resonance spectra were recorded on a Perkin-Elmer R12B machine. ^1H shifts (60 MHz) are listed in ppm to low field of tetramethylsilane, ^{19}F shifts (56.4 MHz) to high field of trichlorofluoromethane, both internal standards. Quoted for each peak are, respectively, the position assigned to the parent atom in the given formula, the intensity (in brackets), the chemical shift, the signal form and the coupling constants (in Hz). AB signal positions are given by $\delta\ \upsilon/2$ from the centre; other signals are b broad, c complex, d doublet, m multiplet, s singlet, t triplet. Unless stated otherwise, the solvent was carbon tetrachloride.

IR spectra (Perkin-Elmer 257 grating instrument) all had bands in the expected regions including those from C–H at ca. 3000 cm^{-1}, but none due to unsaturation.

Mass spectral breakdown patterns were measured on an AEI MS9 machine (70 eV, 200 °C). Significant peaks of structural importance are listed, but when chlorine was present only those based on ^{35}Cl are given.

3.2. Fluorination of 2-chloroethyl methyl ether (I)

A standard reactor [8] was used (96 cm × 16 cm), containing potassium tetrafluorocobaltate (6 kg). Ether **I** [9] (100 g) was passed through dropwise during 2–3 h. Reaction temperatures between 180 and 250 °C gave reasonable results. Contents of cold traps (−78 °C) were poured onto crushed ice, washed with water until neutral and dried ($MgSO_4$). The crude product (ca. 120 g from a typical run) was shown by analytical GLC to contain seven major fractions. GLC separation (6.88 g) in a large column (4.75 m × 3 cm, packing as column A; 112, 22) gave samples of them, which were separated further by GLC to give analytical specimens of the individual compounds isolated, see Table 1.

Compound **II** was 2-chloro-1,1,2,2-tetrafluoroethyl difluoromethyl ether, b.p. 31–32 °C; spectroscopic data were similar to those cited [10].

III was 2-chloro-1,1,2,2-tetrafluoroethyl fluoromethyl ether, b.p. 44–46 °C, having similar spectroscopic parameters to those cited [10].

Table 1
Compounds isolated

Number	Fraction		GLC separation			Compounds[a] present	
	b.p. (°C)	Weight (g)	Unit	°C	N_2		
i	31–32	0.12	A	27	12	**II**	(7)
ii	44–46	0.54	A	52	12	**III**	(10)
iii	56–61	1.11	B	66	12	**IV**	(11)
						V	(11)
iv	77–79	0.32	A	90	15	**VI**	(6)
v	85–87	0.33	A	90	15	**VII**	(12)
vi	85–88	1.25	A	98	15	**VIII**	(12)
						IX	(12)
						I	(trace)
vii	105–110	0.62	A	108	15	**X**	(8)
						XI	(8)

[a] Figures in brackets are total contents of products (%) in the crude mixture from a run at 250 °C, as estimated by GLC.

IV was 2-chloro-1,1,2-trifluoroethyl difluoromethyl ether, b.p. 56–58 °C, with spectroscopic data similar to those cited [11]. *m*/*e*: 118 ($M{-}CF_2O^+$); 117 (116.996357 and 116.973817; $M{-}CHClF^+$ and $M{-}CHF_2O^+$); 99 ($M{-}CF_3O^+$); 67 ($CHClF^+$); 51 (CHF_2^+).

V was 2-chloro-1,2,2-trifluoroethyl difluoromethyl ether, b.p. 59–61 °C. Found: C, 20.1; H, 1.3; Cl, 18.5; F, 51.3. $C_3H_2ClF_5O$ requires C, 19.5; H, 1.1; Cl, 19.2; F, 51.5%. *m*/*e*: 149 (149.000836; $M{-}Cl^+$ requires 149.002574); 117 ($M{-}CHF_2O^+$); 99 ($M{-}CClF_2^+$); 85 ($CClF_2^+$); 51 (CHF_2^+). NMR peaks:

$CF_2H{-}O{-}CFH{-}CF_2Cl$
1 2 34 5

F1 (2) 85.4, 87.2; AB, dd, $J_{A,B}=160$, $J_{1,2}=71.4$, $J_{1,3}\approx6.5$; F3 (1) 140.7; cd, $J_{3,4}=55.8$; F5 (2) 71.5; dd, $J_{3,5}=11.3$, $J_{4,5}=3.6$; H2 (1) 6.45; t, $J_{1,2}=71.4$; H4 (1) 5.87; dt, $J_{3,4}=55.8$, $J_{4,5}=3.6$.

VI was 2-chloro-1,2,2-trifluoroethyl fluoromethyl ether, b.p. 77–79 °C. Found: C, 21.7; H, 1.8; Cl, 21.1; F, 45.9. $C_3H_3ClF_4O$ requires C, 21.6; H, 1.8; Cl, 21.3; F, 45.6%. *m*/*e*: 147 ($M{-}F^+$); 131 ($M{-}Cl^+$); 117 ($M{-}CH_2FO^+$); 85 ($CClF_2^+$); 81 ($M{-}CClF_2^+$); 33 (CH_2F^+). NMR peaks:

$CFH_2{-}O{-}CFH{-}CF_2Cl$
1 2/2' 34 5

F1 (1) 158.3; dddt, $J_{1,2}=53.0$, $J_{1,2'}=48.4$, $J_{1,3}=9.1$, $J_{1,5}=0.8$; F3 (1) 143.3; dtd, $J_{3,4}=59.5$, $J_{3,5}=9.9$, $J_{1,3}=9.1$; F5 (2) 71.2; ddd, $J_{3,5}=9.9$, $J_{4,5}=3.2$, $J_{1,5}=0.8$; H2,2' (2) ca. 5.5; ABX system (c, not analysed); H4 (1) 5.59; dt, $J_{3,4}=59.5$, $J_{4,5}=3.2$.

VII was the known [12] 2-chloro-1,1,2-trifluoroethyl fluoromethyl ether, b.p. 85–87 °C. *m*/*e*: 131 ($M{-}Cl^+$); 117 ($M{-}CH_2FO^+$); 99 ($M{-}CHClF^+$); 83 ($M{-}CHClFO^+$); (33 (CH_2F^+). NMR peaks:

$CFH_2{-}O{-}CF_2{-}CFHCl$
1 2 3 45

F1 (1) 154.6; ttd, $J_{1,2}=53.4$, $J_{1,3}=9.3$, $J_{1,4}=1.4$; F3 (2) 87.3; ddd, $J_{3,4}=11.3$, $J_{1,3}=9.3$, $J_{3,5}=4.8$; F4 (1) 155.1; dtd, $J_{4,5}=48.6$, $J_{3,4}=11.3$, $J_{1,4}=1.4$; H2 (2) 5.56; d, $J_{1,2}=53.4$; H5 (1) 6.09; dt, $J_{4,5}=48.6$, $J_{3,5}=4.8$.

VIII was 2-chloro-1,2-difluoroethyl difluoromethyl ether, b.p. 85–86 °C (stereosiomer A). Found: C, 21.9; H, 1.9; Cl, 21.5; F, 45.9%. *m*/*e*: 131 ($M{-}Cl^+$); 99 ($M{-}CHClF^+$); 83 ($M{-}CHClFO^+$); 79 ($M{-}CHClF_2^+$); 67 (CHF_2O^+); 51 (CHF_2^+). NMR peaks:

$CF_2H{-}O{-}CFH{-}CFHCl$
1 2 34 56

F1 (2) 86.8; cd, $J_{1,2}=72.0$; F3 (1) 135.9; cd, $J_{3,4}\approx56$; F5 (1) 153.5; cd, $J_{5,6}\approx51$; couplings to the ABMX system were not analysed; H2 6.46; t, $J_{1,2}=72$; H4 ca. 5.9; H6 ca. 6.1; ABMX system (not analysed).

IX was 2-chloro-1,2-difluoroethyl difluoromethyl ether, b.p. 86–87 °C (stereoisomer B). Found: C, 21.7; H, 1.9; Cl, 21.7; F, 46.0%. *m*/*e*: peaks were in the same positions as those of stereoisomer A (**VIII**). NMR peaks:

$CF_2H{-}O{-}CFH{-}CFHCl$
1 2 34 56

F1 (2) 85.7; cd, $J_{1,2}=70.8$; F3 (1) 139.1; cd, $J_{3,4}=$ ca 55; F5 (1) 153.3; cd, $J_{5,6}\approx50$; couplings to the ABMX system were not analysed; H2 6.48; t, $J_{1,2}=70.8$; H4 ca. 5.8; H6 ca. 6.1; ABMX system (not analysed).

X was 2-chloro-1,2-difluoroethyl fluoromethyl ether, b.p. 105–107 °C (stereoisomer A). Found: C, 24.5; H, 2.8; Cl, 24.1; F, 38.4. $C_3H_4ClF_3O$ requires C, 24.3; H, 2.7; Cl, 23.9; F, 38.4%. *m*/*e*: 113 ($M{-}Cl^+$); 99 ($M{-}CH_2FO^+$); 81 ($M{-}CHClF^+$); 67 ($CHClF^+$); 49 (CH_2FO^+); 33 (CH_2F^+). NMR peaks (done neat):

$CFH_2{-}O{-}CFH{-}CFHCl$
1 2 34 56

F1 (1) 157.9; cdd, $J_{1,2}\approx56$ and 51; F3 (1) 139.2; cd, $J_{3,4}\approx62$; F5 (1) 153.2; cd, $J_{5,6}\approx51$; couplings to ABX and ABMX systems were not analysed; H2, H4, H6 ca. 5.5, 6.0; ABX and ABMX systems (not analysed).

XI was 2-chloro-1,2-difluoroethyl fluoromethyl ether, b.p. 108–110 °C (stereoisomer B). Found: C, 23.9; H, 2.4; Cl, 23.9; F, 38.2%. *m*/*e*: peaks were in the same positions as those of isomer A (**X**). NMR peaks (done neat):

$CFH_2{-}O{-}CFH{-}CFHCl$
1 2 34 56

F1 (1) 157.3; cdd, $J_{1,2}\approx54$ and 50; F3 (1) 142.8; cd, $J_{3,4}\approx61$; F5 (1) 152.7; cd, $J_{5,6}=$ ca 49; couplings to ABX and ABMX systems were not analysed; H2, H4, H6 ca. 5.5, 6.0; ABX and ABMX systems (not analysed).

When the fluorination of **I** was carried out over cobalt trifluoride in a similar way, in a reactor run at 75–90 °C, total recoveries were only about 25% of those reported above. Compounds **V**–**XI** were isolated from the mixture, and their spectroscopic properties were the same as those recorded above.

3.3. Dehydrohalogenation of 2-chloro-1,2-difluoroethyl difluoromethyl ether (mixed stereoisomers VIII and IX) using potassium hydroxide in benzene

Mixed **VIII** and **IX** (1:1, 0.9 g) were added to powdered KOH (0.7 g) in refluxing benzene (25 ml), in a flask stirred magnetically and fitted with a water condenser and a trap cooled by liquid air. After 4 h, the system was purged by a slow nitrogen stream. The material in the trap (0.1 g) was examined by NMR spectroscopy (Varian XL 100 instrument, ^{1}H at 100 and ^{19}F at 94.1 MHz). A mixture of several vinylic products was indicated, and peaks could be allocated to suggest that (*Z*)-difluoromethyl 1,2-difluorovinyl ether (ca. 50%), and its *E*-stereoisomer (ca. 15%) were present.

$CF_2H{-}O{-}CF{=}CFH$
1 2 3 4 5

Z-isomer (coupling constant values are only approximate). F1 (2) 85.2; dd, $J_{1,2}=72$, $J_{1,3}=5$; F3 (1) 102.7; ddt, $J_{3,4}=19$, $J_{3,5}=12$, $J_{1,3}=5$; F4 (1) ca. 172; dd, $J_{4,5}=71$, $J_{3,4}=19$; H2 6.31; t, $J_{1,2}=72$; H5 6.46; dd, $J_{4,5}=71$, $J_{3,5}=13$.

E-isomer. F1 (2) 83.8; ddd, $J_{1,2}=72$; F3 (1) 128.5; cd, $J_{3,4}=124$; F4 (1) ca. 182; cdd, $J_{3,4}=124$, $J_{4,5}=71$; H2 6.38; t, $J_{1,2}=72$; H5 6.81; dd, $J_{4,5}=71$.

3.4. Chlorination of 2-chloro-1,2-difluoroethyl difluoromethyl ether (mixed stereoisomers VIII and IX)

Mixed **VIII** and **IX** (1:1, 4.5 g) and chlorine (9.8 g), sealed in a Carius tube (105 ml), were irradiated with UV light (medium pressure Hanovia lamp) for 63 h. The product (6.2 g) was washed and dried, and was separated (5.1 g) by GLC (C, 117, 9) to give pure components (i)–(iv), and mixtures (a)–(d).

Component (i) was 1,2,2-trichloro-1,2-difluoroethyl difluoromethyl ether (**XII**), b.p. 105–107 °C (1.42 g). Found: C, 15.3; H, 0.4; Cl, 45.6; F, 32.2. $C_3HCl_3F_4O$ requires C, 15.3; H, 0.4; Cl, 45.2; F, 32.3%. *m/e*: 199 ($M{-}Cl^+$); 167 ($M{-}CHF_2O^+$); 133, ($M{-}CCl_2F^+$); 113 ($C_2ClF_2O^+$); 101 (CCl_2F^+); 51 (CHF_2^+). NMR peaks:

$CF_2H{-}O{-}CFCl{-}CFCl_2$
1 2 3 4

F1 (2) 84.9, 86.5; ABdd, $J_{A,B}=180$, $J_{1,2}\approx 69$, $J_{1,3}=5.3$; F3 (1) 70.2; dt, $J_{3,4}=11.6$, $J_{1,3}=5.3$; F4 (1) 71.9; d, $J_{3,4}=11.6$; H (2) 6.81; dd, $J_{1,2}=68.4, 69.6$.

Product (ii) was 1,2,2-trichloro-1,2-difluoroethyl chlorodifluoromethyl ether (**XIII**), b.p. 115–116 °C (0.26 g). Found: C, 13.4; Cl, 52.8; F, 28.5. $C_3Cl_4F_4O$ requires C, 13.4; Cl, 52.6; F, 28.2%. *m/e*: 233 ($M{-}Cl^+$); 167 ($M{-}CClF_2O^+$); 132, ($M{-}CCl_2F_2O^+$); 117 (CCl_2FO^+); 101 (CCl_2F^+); 85 ($CClF_2^+$). NMR peaks:

$CF_2Cl{-}O{-}CFCl{-}CFCl_2$
1 2 3

F1 (2) 26.6, 27.5; ABd, $J_{A,B}=89$, $J_{1,2}=12.1$; F2 (1) 75.3; td, $J_{1,2}=12.1$, $J_{2,3}=11.3$; F3 (1) 72.2; d, $J_{2,3}=11.3$.

Compound (iii) was pentachloroethyl difluoromethyl ether (**XIV**), b.p. 170–172 °C (0.04 g). *m/e*: 230.879415 ($M{-}Cl^+$ requires 230.874963); 199 ($M{-}CHF_2O^+$); 117 (CCl_3^+); 51 (CHF_2^+). NMR peaks (done neat):

$CF_2H{-}O{-}CCl_2{-}CCl_3$
1 2

F1, 85.8; d, $J_{1,2}=69.6$; H2, 7.00; d, $J_{1,2}=69.6$

Product (iv) was hexachloroethane (**XV**), m.p. 65–67 °C (subl.), with a correct IR spectrum.

NMR and MS spectra suggested the presence of the following compounds in the mixtures isolated: (a) $CCl_2FCCl_2OCHF_2$ (**XVI**) and $CCl_3CClFOCHF_2$ (**XVII**) (5:2); (b) $CCl_2FCCl_2OCClF_2$ (**XVIII**) and $CCl_3CF_2OCCl_2F$ (**XIX**, this may have arisen from the presence of **VII** as an impurity in **VIII**+**IX**); (c) product not identified; (d) $CCl_2FCClFOCCl_3$ (**XX**). It must be emphasized that these structures for **XVI–XX**, though probable, were not established rigorously.

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