Journal of Fluorine Chemistry, 4 (1974) 387 - 397
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ELECTROCHEMICAL FLUORINATION OF CHLORINE-CONTAINING ETHERS

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(Received September 19, 1973)

Summary

The electrochemical fluorination of chlorine-containing ethers has been studied. In general, it was found that a chlorine bonded to an α–carbon atom in the ethers was readily removed during electrochemical reaction in anhydrous hydrogen fluoride, whilst a chlorine bonded to the β–carbon atom was retained to yield β–chlorinated polyfluoroethers.

Through the use of this method, several new chloropolyfluoroethers, *e.g.* 2-chloro-1,1,2,2-tetrafluoroethyl difluoromethyl ether, 2,2-dichloro-1,1,2-trifluoroethyl trifluoromethyl ether, 2,2-dichloro-1,1,2-trifluoroethyl difluoromethyl ether, 2,2-dichloro-1,1,2-trifluoroethyl chlorodifluoromethyl ether, 2-chloro-1,1,2,2-tetrafluoroethyl chlorodifluoromethyl ether and 2,2-trichloro-1,1-difluoroethyl trifluoromethyl ether, have been isolated and characterized.

Introduction

The present paper deals with the electrochemical fluorination of chlorine-containing dimethyl, methyl ethyl and vinyl ethers. The replacement of a hydrogen by a fluorine is known to be favored over the replacement of a chlorine by a fluorine during the electrochemical fluorination of halogenohydrocarbons [1] and it appeared to be of interest to examine whether this behaviour persists during the electrochemical fluorination of chlorinated ethers. This work was also directed towards the possible use of this method for the preparation of chlorine-containing polyfluoroethers that are usually difficult to prepare in one step from chlorohydrocarbon ethers by conventional methods [2]. In a previous study [3], it was shown that chlorine attached to an aromatic nucleus was retained during electrochemical fluorination; thus chloropolyfluorocyclohexyl ether was found amongst the products resulting from the fluorination of a chlorinated aromatic ether.

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Results and discussion

Although a considerable amount of work has been undertaken on the electrochemical fluorination of the hydrocarbon ethers, little information is yet available on the fluorination of chlorinated ethers [4]. The present work is an attempt to clarify the behaviour of chlorine-containing ethers during electrochemical fluorination and for this reason the behaviour of chlorinated dimethyl ethers was first studied. The following ethers were included in this investigation: chloromethyl methyl, bis(chloromethyl), dichloromethyl chloromethyl, trichloromethyl methyl and bis(dichloromethyl).

It was found that the chlorine atoms in dimethyl ethers were very readily replaced by fluorine to give bis(trifluoromethyl), trifluoromethyl difluoromethyl and bis(difluoromethyl) ethers, and trifluoromethyl methyl ether (from trichloromethyl methyl ether), as the principal products, together with fragmented fluoro- and chlorofluoro-carbons and carbonyl fluoride. Only two chlorine-containing fluoroethers were isolated from the fluorination products of dimethyl ethers; chlorofluoromethyl difluoromethyl ether (0.6% yield) from dichloromethyl chloromethyl ether and chlorodifluoromethyl methyl ether (13.2% yield) from trichloromethyl methyl ether. The chlorine atoms in these ethers were found to be displaced as chlorine gas or as hydrogen chloride during the fluorination process.

The results obtained during the electrochemical fluorination of dichloromethyl chloromethyl ether are given below (in the Experimental section) as a representative example of the fluorination of chlorinated dimethyl ethers. The ready loss of chlorine atoms from dimethyl ethers may be explained in terms of an ionic reaction between the ethers and hydrogen fluoride to form fluoroethers *via* a resonance-stabilized carbonium ion, this fluorination process occurring simultaneously with the electrochemical process which proceeds *via* a radical mechanism.

In a subsequent study, the electrochemical fluorination of β–chlorinated ethyl methyl ethers was examined to see whether the chlorine atom attached to the β–carbon atom would be retained in the molecule during fluorination. In order to reduce the tendency of the ether linkage to undergo cleavage, *a,a*– difluorinated ethers were chosen as starting materials. Thus 2-chloro-1,1,2-trifluoroethyl methyl ether [5] and its chlorinated derivatives, *i.e.* 2-chloro-1,1,2-trifluoroethyl chloromethyl, 2-chloro-1,1,2-trifluoroethyl dichloromethyl, 2-chloro-1,1,2-trifluoroethyl trichloromethyl, 2,2-dichloro-1,1,2-trifluoroethyl dichloromethyl and 2,2-dichloro-1,1,2-trifluoroethyl trichloromethyl ether, were fluorinated. It was anticipated that this fluorination would also serve as a method [6] for the preparation of chlorine-containing polyfluoroethers from chlorofluoroethers with low degrees of fluorination.

The results obtained are summarized in Table 1. Chlorine atoms attached to β–carbon atoms were retained in the molecules giving β–chlorinated polyfluoroethers, including several new compounds, in a total yield of up to 80%. Hydrogen atoms attached to β–carbon atoms were displaced in preference to chlorine. The new ethers obtained in this way included 2-chloro-1,1,2,2-tetrafluoroethyl difluoromethyl (b. p. 29 °C), 2,2-dichloro-1,1,2-trifluoroethyl trifluoromethyl (b.p. 42 °C), 2,2-dichloro-1,1,2-trifluoroethyl difluoromethyl (b. p. 64 °C), 2,2-dichloro-1,1,2-trifluoroethyl chlorodifluoromethyl (b. p. 78°C) and 2-chloro-1,1,2,2-tetrafluoroethyl chlorodifluoromethyl ether (b. p. 43 °C). The last two ethers in which chlorine is retained at the methyl group were mainly derived from trichloromethyl ethers, *i.e.* 2-chloro-1,1,2-trifluoroethyl trichloromethyl or 2,2-dichloro-1,1,2-trifluoroethyl trichloromethyl ether.

The kinds and amounts of the products obtained indicate that the reaction proceeds by means of a radical mechanism and involves the stepwise and progressive replacement of hydrogen and chlorine atoms by fluorine. In general, ethers which have a larger number of chlorine atoms appear to be more stable during fluorination, exhibiting a much lower tendency towards fragmentation. This may be partly explained in terms of the heat of reaction associated with the fluorination process; the replacement of hydrogen by fluorine is more highly exothermic than that of chlorine and will thus be accompanied by an increased tendency for cleavage of the ether molecule. Of such ethers, perhalogenated ethers, and in particular 2,2-dichloro-1,1,2-trifluoroethyl trichloromethyl ether, gave a high yield (80%) of chloropolyfluoro ethers.

Finally, the electrochemical fluorination of β,β,β-trichlorinated ethers, *e.g.* 2,2,2-trichloroethyl methyl, 1,2,2,2-tetrachloroethyl methyl and pentachloroethyl methyl ethers, has been studied. The results obtained are listed in Table 2. Although the yield of chloropolyfluoroethers was low (total yield, 15 - 25%) and extensive fragmentation was observed, in all cases ethers containing a β-chlorine atom were obtained. Thus, 2,2,2-trichloro-1,1-difluoroethyl trifluoromethyl ether (b. p. 76 °C) was isolated from the fluorination products of 2,2,2-trichloroethyl methyl and 1,2,2,2-tetrachloroethyl methyl ethers.

Since the initial ethers contained no fluorine and were not stabilized, cleavage of the ether molecules during fluorination was more extensive, and in addition to fluoro- and chlorofluoro-carbons and carbonyl fluoride some trihalogenoacyl fluorides were formed [7]. These included trifluoroacetyl, chlorodifluoroacetyl and dichlorofluoroacetyl fluorides but no evidence was found for the formation of trichloroacetyl fluoride.

The behaviour of chlorinated unsaturated ethers, *e.g.* 1,2,2-trichlorovinyl methyl and 2,2-dichlorovinyl methyl ethers, during fluorination has also been studied in the present work. The results obtained are also included in Table 2. It is probable that during the electrochemical fluorination of such olefinic compounds addition of fluorine to the double bond occurs initially [3] followed by the replacement of hydrogen and chlorine atoms by fluorine. It was found that the trichlorovinyl methyl ether, which probably produces a perhalogenated ethyl methyl ether as an intermediate, gave the best results and led to the formation of reasonable amounts of β-chlorinated polyfluoroethers in a total yield of 59%.

TABLE 2

Fluorination of 2,2,2-trichloroethyl methyl ether and its chlorinated derivatives, and chlorinated vinyl methyl ethers

Conditions					
Materials	$CH_3OCH_2CCl_3$	$CH_3OCHClCCl_3$	$CH_3OCCl_2CCl_3$	$CH_3OCCl{=}CCl_2$	$CH_3OCH{=}CCl_2$
Amount used (mol)	0.200	0.200	0.100	0.200	0.200
Quantity of electricity (A h)	76	76	36	58	79
Time (min)	230	215	125	245	233
Cell temp (°C)	7 - 10	6 - 7	19 - 20	8 - 10	8 - 9
He flow (cm^3 min^{-1})	150	150	150	150	150
Results					
Products (g) A[a]	33.0	33.4	7.5	37.5	26.6
B[b]	5.0	5.5	2.9	1.1	3.3
Product yield (%)					
C_1 compounds	79.0	81.2	38.4	24.5	75.5
C_2 compounds	0.8	2.9	1.7	2.5	1.6
C–O–C compounds	10.2	8.3	1.5	5.8	4,5
$CF_3OC_2F_5$	2.3	4.4	1.5	7.6	3.5
$CF_3OCF_2CClF_2$	8.3	4.8	1.8	15.0	8.6
$CHF_2OCF_2CClF_2$	2.3	0.2	4.9	5.2	0.7
$CF_3OCF_2CCl_2F$	7.9	13.5	2.9	28.9	4.8
$CHF_2OCF_2CCl_2F$	1.9	3.4	5.0	9.8	
$CClF_2OCF_2CCl_2F$			0.4		0.5
$CF_3OCF_2CCl_3$	1.0	3.0			
Others[c]	4.5	0.8	0.3	0.7	4.3
CF_3COONa	2.0	2.8	8.0	2.2	4.5
$CClF_2COONa$	6.1	3.1	9.2	0.7	3.8
$CCl_2FCOONa$	7.7	11.2	2.4	0.9	2.7

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[a] Fluorocarbons and fluoroethers.

[b] Sodium salts.

[c] Given in gram units.

Experimental

The electrolytic cell used was similar to that described previously [8]. Analytical gas chromatography was carried out with a Shimadzu GC-4A chromatograph using a 2 m stainless-steel column (3 mm diam.) packed with silica gel (60 - 80 mesh) (Col. A), and a 4 m column (3 mm diam.) packed with 25% of Daifl oil 3 on Chromosorb P-AW (60 - 80 mesh) (Col. B), 25% of Daifl oil 10 on Chromosorb P-AW (Col. C), or 15% of Silicone DC QF-1 on Chromosorb P-AW (Col. D). For semi-preparative work, a Shimadzu GC-1C chromatograph was used with a 10 m column (6 mm diam.) packed with 25% of Daifl oil 10 on C-22 (60 - 80 mesh) or 25% of Silicone DC QF-1 on Chromosorb P-AW. The carrier gas was helium in all cases.

Infrared spectra were recorded on a Hitachi EPI-S2 spectrometer using a gas cell equipped with NaCl windows, and mass spectra on a Hitachi RMU-7 instrument at 70 eV. The ^{19}F and ^{1}H NMR spectra were measured with a JEOL C-60 instrument at 56.4 MHz and 60 MHz with CF_3 COOH (external) and TMS (internal), respectively, as references. The values quoted are chemical shifts (δ) and are in ppm relative to the respective references.

With the exception of chloromethyl methyl ether (Tokyo Chemical Industry Co.) and 2-chloro-1,1,2-trifluoroethyl methyl ether (Pierce Chemical Co.), the starting materials, *i.e.* bis(chloromethyl), dichloromethyl chloromethyl, bis(dichloromethyl) [9], trichloromethyl methyl [10], 2-chloro-1,1,2-trifluoroethyl chloromethyl, 2-chloro-1,1,2-trifluoroethyl dichloromethyl, 2-chloro-1,1,2-trifluoroethyl trichloromethyl, 2,2-dichloro-1,1,2-trifluoroethyl dichloromethyl, 2,2-dichloro-1,1,2-trifluoroethyl trichloromethyl [11], 2,2,2-trichloroethyl methyl [12] (by the reaction of 2,2,2-trichloroethanol with dimethyl sulfate), 1,2,2,2-tetrachloroethyl methyl [13], pentachloroethyl methyl, 1,2,2-trichlorovinyl methyl [14] and 2,2-dichlorovinyl methyl [13] ether, were prepared according to procedures described in the literature. Anhydrous hydrogen fluoride was more than 99.5% pure.

Fluorination of chlorinated dimethyl ethers

As an example of the electrochemical fluorination of chlorinated dimethyl ethers, the fluorination of dichloromethyl chloromethyl ethers is described. To electrically purified anhydrous hydrogen fluoride (450 cm^3) contained in a 650 cm^3 cell, dichloromethyl chloromethyl ether (36.8 g, 0.246 mol) was added over a period of 30 min by means of a mechanical micropump. This process was accompanied by the continuous passage of an electric current, the average anodic current density being 2.4 A dm^{-2}(effective surface areas of the anodes and the cathodes were each 7.7 dm^2) with a cell voltage of 6.4 - 6.8 V and a cell temperature of 7 - 8 °C. Helium (100 cm^3 min^{-1}) was passed into the cell through a bubbler fitted in its bottom. The total quantity of electricity passed was 40 A h over a period of 130 min. At the end of the electrolysis the voltage rose to 9.0 V. The passage of helium was continued for a further 60 min after the completion of electrolysis.

The gaseous products evolving from the cell were passed through the reflux condenser maintained at −15 °C, and then consecutively through a sodium fluoride tube, gas-washing bottles filled with a 10% aqueous solution of sodium hydroxide and potassium sulfite containing a small amount of potassium iodide (in order to absorb carbonyl fluoride and oxygen difluoride) and finally a series of cold traps immersed in ice and in liquid nitrogen [8].

The products (21.2 g) which collected in the cold traps were combined and then separated into five fractions by the use of a low-temperature rectification unit. Each fraction was then further subjected to the following gas chromatographic analysis (compositions were calculated on the basis of chromatographic peak areas, assuming, as usual, equal weight sensitivities for all components): fraction 1, −128 °C to −127 °C, 4.4 g (Col. A, 100 °C); fraction 2, −85 °C to −80 °C, 3.3 g (Col. A, 130 °C); fraction 3, −58 °C to −57 °C, 3.0 g (Col. A, 130 °C; Col. B, 25 °C); fraction 4, −38 °C to 0 °C, 4.7 g (Col. A, 130 °C; Col. B, 0 °C); fraction 5 (residue), 5.6 g (Col. B, 25 °C). The following compounds were obtained: CF_4 (4.4 g), CHF_3 (3.2 g), $CClF_3$ (0.1 g), CCl_2F_2 (0.5 g), $CHCl_2F$ (0.2 g), C_3F_8 (0.1 g), CF_3OCF_3 (3.1 g), CHF_2OCF_3 (2.6 g), CHF_2OCHF_2 (6.0 g), CH_2FOCHF_2 (0.5 g), $CHF_2OCHClF$ (0.2 g), and others (0.1 g).

Chlorodifluoromethyl methyl ether obtained in the electrochemical fluorination of trichloromethyl methyl ether (which was found to react with anhydrous hydrogen fluoride alone to yield chlorodifluoromethyl methyl and trifluoromethyl methyl ethers, together with hydrogen chloride) had b.p. 17 °C (lit. value [15]: 55.3 °C). (All boiling points are uncorrected). Its IR spectrum had absorption bands at 3000 (w, sh), 2970 (w), 2870 (w), 1466 (m), 1242 (vs), 1186 (m, sh), 1181 (m), 1173 (m), 1152 (s), 1143 (s), 1135 (s, sh), 1096 (s), 1074 (s), 1064 (s), 1057 (s, sh), 1008 (vs), 1002 (vs), 743 (m), 735 (m) and 727 (m, sh) cm^{-1}. The ^{19}F NMR spectrum (CCl_4) of this compound exhibited a singlet at −47.3. The ^1H NMR spectrum exhibited a singlet at 4.3. The mass spectrum had peaks at 115 $[M - H]$, 101 $[M - CH_3]$, 97 $[M - F]$, 85 $[CClF_2]$ and 81 $[M - Cl]$. Analysis: Found: C, 20.45; H, 2.56; Cl, 30.8; F, 32.4%. $C_2H_3ClF_2O$ requires C, 20.62; H, 2.59; Cl, 30.4; F, 32.6%.

Fluorination of 2-chloro-1,1,2-trifluoroethyl methyl ether and its chlorinated derivatives

The electrochemical fluorination of 2,2-dichloro-1,1,2-trifluoroethyl dichloromethyl ether is described as an example, the procedure employed being virtually identical to that described above. The sample (20.2 g, 0.080 mol) was fed into the cell and electrolyzed using an average anodic current density of 1.9 A dm^{-2}, the cell voltage being 6.5 - 8.0 V and the cell temperature 7 - 8 °C. A total quantity of electricity of 34 A h was supplied over a period of 140 min. The flow rate of helium was 150 cm^3 min^{-1}.

The products (15.8 g) condensed in the cold traps were distilled into three fractions and subjected to gas chromatography: fraction 1, −24 °C to −23 °C, 2.6 g (Col. A, 130 °C); fraction 2, 10 °C to 11 °C, 5.3 g (Col. C, 23 °C);

fraction 3 (residue), 7.8 g (Col. D, 20 °C to 100 °C, programed 4 °C min^{-1}). The following compounds were found: CF_4 (trace), $CClF_3$ (0.1 g), $CHClF_2$ (0.1 g), C_2F_6 (trace), CCl_2FCF_3 (0.1 g), $CF_3OC_2F_5$ (3.2 g), $CHF_2OC_2F_5$ (0.2 g), $CF_3OCF_2CClF_2$(4.9 g), $CHF_2OCF_2CClF_2$ (3.0 g), $CF_3OCF_2CCl_2F$ (2.4 g), $CHF_2OCF_2CCl_2F$ (1.3 g), $CClF_2OCF_2CCl_2F$ (0.3 g), and others (0.1 g).

2-Chloro-1,1,2,2-tetrafluoroethyl difluoromethyl ether had b. p. 29 °C and $n_D^{20} < 1.28$. Its IR spectrum had absorption bands at 3027 (w), 1405 (w), 1350 (m), 1220 (s), 1181 (vs), 1170 (vs, sh), 1133 (vs), 1078 (s), 1051 (s), 970 (s), 839 (m), 815 (m), 791 (w) and 693 (w) cm^{-1}. The ^{19}F NMR spectrum (neat) of this compound exhibited signals centered at +8.6 (CHF_2–, doublet of triplets), +11.3 (–CF_2–, multiplet) and –2.7 ($CClF_2$–, unresolved triplet). The ^1H NMR spectrum exhibited a triplet centered at 6.5 [J(HF) = 69 Hz]. The mass spectrum had peaks at 201 [M – H], 183 [M – F], 151 [M – CHF_2], 135 [M –CHF_2O], 117 [M – $CClF_2$] and 100 [C_2F_4]. Analysis: Found: C, 17.23; H, 0.50; Cl, 17.2; F, 55.8 %. C_3HClF_6O requires C, 17.79; H, 0.50; Cl, 17.5; F, 56.3%.

2,2-Dichloro-1,1,2-trifluoroethyl trifluoromethyl ether had b. p. 42 °C and n_D^{20} 1.2985. Its IR spectrum had absorption bands at 1370 (w), 1381 (s), 1258 (vs), 1239 (vs), 1149 (vs), 1104 (s), 969 (w), 950 (m), 909 (s), 874 (m), 842 (m), 812 (m), 688 (w) and 663 (m) cm^{-1}. The ^{19}F NMR spectrum (neat) of this compound exhibited signals centered at –21.3 (CF_3–, triplet), +10.6 (–CF_2–, multiplet) and –0.6 (CCl_2F–, triplet). The mass spectrum had peaks at 201 [M – Cl], 151 [M – CF_3O], 135 [M – CCl_2F] and 101 [CCl_2F], Analysis: Found: C, 15.07; Cl, 29.7; F, 47.9%. $C_3Cl_2F_6O$ requires C, 15.21; Cl, 29.9; F, 48.1%.

2,2-Dichloro-1,1,2-trifluoroethyl difluoromethyl ether had b. p. 64 °C and n_D^{20} 1.3241. Its IR spectrum had absorption bands at 3020 (w), 1405 (w), 1368 (w), 1304 (s), 1212 (s), 1164 (vs), 1123 (vs), 1073 (vs), 1050 (m), 930 (m), 906 (s), 823 (w) and 800 (m) cm^{-1}. The ^{19}F NMR spectrum (neat) of this compound exhibited signals centered at +7.8 (CHF_2–, doublet of triplets, one of which overlapped the signals of –CF_2–), +8.6 (–CF_2–, multiplet) and –1.3 (CCl_2F–, triplet). The ^1H NMR spectrum exhibited a triplet centered at 6.5 [J(HF)= 69 Hz]. The mass spectrum had peaks at 217 [M – H], 183 [M – Cl], 151 [M – CHF_2O], 117 [M – CCl_2F] and 101 [CCl_2F]. Analysis: Found: C, 16.44; H, 0.43; Cl, 32.2; F, 43.1%. $C_3HCl_2F_5O$ requires C, 16.46; H, 0.46; Cl, 32.4; F, 43.4%.

2,2-Dichloro-1,1,2-trifluoroethyl chlorodifluoromethyl ether had b. p. 78 °C and n_D^{20} 1.3389. Its IR spectrum had absorption bands at 1294 (s), 1211 (vs), 1136 (vs), 1121 (vs), 1094 (s), 1064 (s), 1056 (s, sh), 932 (s), 911 (s), 825 (w), 806 (m), 755 (w) and 743 (m) cm^{-1}. The ^{19}F NMR spectrum (neat) of this compound exhibited signals centered at –51.6 ($CClF_2$–, triplet), +9.5 (–CF_2–, triplet of doublets) and –1.5 (CCl_2F–, triplet). The mass spectrum had peaks at 217 [M – Cl], 151 [M – $CClF_2O$], 116 [C_2ClF_3] and 101 [CCl_2F]. Analysis: Found: C, 14.07; Cl, 42.3; F, 37.1%. $C_3Cl_3F_5O$ requires C, 14.22; Cl, 42.0; F. 37.5%.

Pentafluoroethyl difluoromethyl ether could only be characterized spectroscopically because of its small amount. Its IR spectrum had absorption bands at 3020 (m), 1405 (m), 1370 (m), 1243 (vs), 1175 (s), 1125 (vs), 1034 (m), 859 (m) and 752 (m) cm^{-1}. The ^{19}F NMR spectrum (CCl_4) of this compound exhibited signals centered at +5.7 (CHF_2–, doublet of triplets), + 10.3 (–CF_2–, multiplet) and +7.8 (CF_3–, broad singlet). The ^{1}H NMR spectrum exhibited a triplet centered at 6.5 [J(HF) = 68 Hz]. The mass spectrum had peaks at 186 [M], 185 [M − H], 167 [M − F], 119 [M − CHF_2O] and 117 [M − CF_3].

In addition, as shown in Table 1, the following new compounds were isolated and identified during the fluorination of this class of chlorofluoroethers. When the amounts of compounds isolated were small, only spectroscopic data were obtained.

2-Chloro-1,1,2,2-tetrafluoroethyl chlorodifluoromethyl ether had b. p. 43 °C and n_D^{20} 1.2954. Its IR spectrum had absorption bands at 1339 (s), 1320 (m), 1259 (s, sh), 1212 (vs), 1189 (vs), 1144 (vs), 1123 (s, sh), 1067 (s), 1056 (s), 974 (s), 912 (w), 843 (m), 825 (m), 778 (m) and 757 (m) cm^{-1}. The ^{19}F NMR spectrum (neat) of this compound exhibited signals centered at −51.6 ($CClF_2$–O, triplet), +12.1 (–CF_2–, triplet) and −2.7 ($CClF_2$–C, broad singlet). The mass spectrum had peaks at 201 [M − Cl], 135 [M − $CClF_2O$] and 100 [C_2F_4]. Analysis: Found: C, 14.86; Cl, 30.2; F, 47.7%. $C_3Cl_2F_6O$ requires C, 15.21; Cl, 29.9, F, 48.1%.

1,1,2,2-Tetrafluoroethyl difluoromethyl ether: its IR spectrum had absorption bands at 3010 (w, sh), 2986 (w), 1403 (w), 1364 (w), 1298 (m), 1209 (s), 1160 (vs), 1142 (vs), 1073 (m), 1053 (m), 870 (w), 799 (m) and 740 (w) cm^{-1}. The ^{19}F NMR spectrum (CCl_4) of this compound exhibit signals centered at +5.6 (CHF_2–O, doublet of triplets), +10.5 (–CF_2–, multiplet) and +59.8 (CHF_2–C, doublet of triplets). The ^{1}H NMR spectrum exhibited a triplet centered at 6.5, partly overlapping the signals of CHF_2C– [CHF_2–O, J (HF) = 68 Hz] and a triplet of triplets centered at 5.6 [CHF_2–C, $J(HF)_{gem}$ = 51 Hz, $J(HF)_{vic}$ = 3 Hz]. The mass spectrum had peaks at 167 [M − H], 117 [M − CHF_2] and 101 [M − CHF_2O].

2-Chloro-1,1,2,2-tetrafluoroethyl fluoromethyl ether: its IR spectrum had absorption bands at 3035 (w), 2955 (w), 1368 (m), 1291 (m), 1214 (vs), 1180 (vs), 1155 (vs), 1129 (vs), 1067 (s, sh), 1050 (vs, sh), 1031 (vs), 958 (s), 935 (m) and 776 (m) cm^{-1}. The ^{19}F NMR spectrum (CCl_4) of this compound exhibited signals centered at +77.1 (CH_2F–, triplet of triplets), + 11.0 (–CF_2–, doublet of triplets) and −5.1 ($CClF_2$–, unresolved triplet). The ^{1}H NMR spectrum exhibited a doublet centered at 5.6 [J(HF) = 50 Hz]. The mass spectrum had peaks at 183 [M − H], 165 [M − F], 149 [M − Cl], 135 [M − CH_2FO] and 99 [M − $CClF_2$].

2-Chloro-1,1,2-trifluoroethyl chlorodifluoromethyl ether: its IR spectrum had absorption bands at 3000 (w), 1372 (m), 1300 (s), 1271 (s), 1187 (vs), 1129 (vs), 1063 (s), 890 (m), 845 (m), 834 (m), 775 (m), 758 (w, sh), 734 (w), 722 (w), 698 (w) and 684 (w) cm^{-1}. The ^{19}F NMR spectrum (neat) of this compound exhibited signals centered at −52.3 ($CClF_2$−, triplet), +9.0 (−CF_2−, multiplet) and +79.2 (CHClF−, doublet of triplets). The ^1H NMR spectrum exhibited a doublet of triplets centered at 6.2 [$J(HF)_{gem}$ = 48 Hz, $J(HF)_{vic}$ = 5 Hz]. The mass spectrum had peaks at 217 [M − H], 183 [M − Cl], 151 [M − CHClF], 117 [M − $CClF_2O$] and 101 [$CClF_2O$].

2-Chloro-1,1,2,2-tetrafluoroethyl dichlorofluoromethyl ether was obtained as a mixture of 2,2-dichloro-1,1,2-trifluoroethyl chlorodifluoromethyl ether. Its ^{19}F NMR spectrum (neat) exhibited signals centered at −67.0 (CCl_2F−, triplet), +11.0 (−CF_2−, doublet of triplets) and −3.4 ($CClF_2$−, unresolved triplet).

Fluorination of 2,2,2-trichloroethyl methyl ether and its chlorinated derivatives, and chlorinated vinyl methyl ethers

The electrochemical fluorination of 1,2,2,2-tetrachloroethyl methyl ether is described as an example. 1,2,2,2-Tetrachloroethyl methyl ether (39.8 g, 0.200 mol) was added to the cell by means of a micropump accompanied by the passage of an electric current, the average anodic current density being 2.8 A dm^{-2} with a cell voltage of 5.8 - 8.0 V and a cell temperature of 6 - 7 °C. A total quantity of 76 A h of electricity was supplied over a period of 215 min. The flow rate of helium was 150 cm^3 min^{-1}.

The products (33.4 g) condensed in the cold traps were distilled into five fractions and subjected to gas chromatography: fraction 1, −128 °C, 3.6 g (Col. A, 100 °C); fraction 2, −84 °C to −73 °C, 5.2 g (Col. A, 100 °C); fraction 3, −25 °C to −22 °C, 4.7 g (Col. A, 130 °C); fraction 4, 0 °C to 11 °C, 4.7 g (Col. B, 19 °C; Col. C, 23 °C); fraction 5 (residue), 15.0 g (Col. C, 50 °C; Col. D, 60 °C). In addition to fluorocarbon products, fluorination of ethers in this category yielded trihalogenoacyl fluorides as the result of cleavage of the carbon−oxygen bond of the methoxyl group in the ethers. The acyl fluorides in the mixture of gaseous products generated from the cell were converted into the corresponding halogenated acids by bubbling through water contained in a pair of polyethylene bottles connected next to the sodium fluoride tube. The acids thus formed were isolated as the sodium salts (5.5 g) by the method described earlier [7] and analyzed by ^{19}F NMR spectroscopy.

The following compounds were obtained: CF_4 (3.6 g), CHF_3 (4.0 g), $CClF_3$ (0.8 g), CCl_2F_2 (2.8 g), CCl_3F (4.6 g), C_2F_6 (0.1 g), $CClF_2CClF_2$ (0.1 g), CCl_2FCF_3 (0.2 g), CCl_2FCClF_2 (0.4 g), CCl_3CF_3 (0.2 g), CF_3OCF_3 (0.8 g), CHF_2OCF_3 (0.2 g), CHF_2OCHF_2(1.2 g), $CF_3OC_2F_5$ (1.8 g), CF_3OCF_2-$CClF_2$ (2.1 g), $CHF_2OCF_2CClF_2$ (0.1 g), $CF_3OCF_2CCl_2F$ (6.4 g), CHF_2OCF_2-CCl_2F (1.5 g), $CF_3OCF_2CCl_3$ (1.5 g), and others (0.8 g). The sodium salts of the halogenated acids were found to consist of a mixture of CF_3COONa (0.8 g), $CClF_2COONa$ (0.9 g) and $CCl_2FCOONa$ (3.8 g).

2,2,2-Trichloro-1,1-difluoroethyl trifluoromethyl ether had b. p. 76 °C and n_D^{20} 1.3415. Its IR spectrum had absorption bands at 1304 (s), 1243 (vs), 1238 (vs, sh), 1225 (s, sh), 1181 (m), 1144 (s), 870 (m, sh), 860 (m), 830 (w), 798 (w) and 664 (w) cm^{-1}. The ^{19}F NMR spectrum (neat) of the compound exhibited signals centered at —21.3 (CF_3–, triplet) and —7.3 (–CF_2–, quartet). The mass spectrum had peaks at 217 [M — Cl], 167 [M — CF_3O], 135 [M — CCl_3], 117 [CCl_3] and 113 [C_2ClF_2O]. Analysis: Found: C, 14.13; Cl, 42.1; F, 37.0%. $C_3Cl_3F_5O$ requires C, 14.22; Cl, 42.0; F, 37.5%.

Acknowledgements

The authors wish to thank the Daikin Industries Corporation for supplying anhydrous hydrogen fluoride.

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