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POLYFLUORO DIETHYL AND ETHYL METHYL ETHERS: THEIR PREPARATION USING COBALT (III) FLUORIDE AND POTASSIUM TETRAFLUOROCOBALTATE (III) AND THEIR DEHYDROFLUORINATION

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SUMMARY

Diethyl ether has been fluorinated with CoF_3 to yield a mixture from which dl -threo and -erythro 1,2-difluoroethyl 1,2,2-trifluoroethyl ether, dl and meso bis(1,2,2-trifluoroethyl) ether and dl-1,1,2,2-tetrafluoroethyl 1,2,2-trifluoroethyl ether were isolated. Fluorination with $KCoF_4$ at ca 200° afforded ethyl 1,2,2-trifluoroethyl ether as the sole isolable product; at higher temperatures some of the above ethers were formed. Similar fluorinations with CoF_3 of ethyl methyl ether afforded 1,2,2-trifluoroethyl methyl ether, 1,2,2-trifluoroethyl fluoromethyl ether, 1,2,2-trifluoroethyl difluoromethyl ether and 1,1,2,2-tetrafluoroethyl methyl ether; with $KCoF_4$ 1,2,2-trifluoroethyl methyl ether was the sole product. Dehydrofluorination, using fused potassium hydroxide, of either isomer of bis(1,2,2-trifluoroethyl) ether gave a mixture of (E, Z) and (Z, Z) bis(1,2-difluorovinyl) ethers and (E) and (Z) 1,2,2-trifluoroethyl 1,2-difluorovinyl ethers. Similarly, 1,1,2,2-tetrafluoroethyl 1,2,2-trifluoroethyl ether yielded (E) and (Z) 1,1,2,2-tetrafluoroethyl 1,2-difluorovinyl ether in the ratio 1:4. Dehydrofluorination of 1,2,2-trifluoroethyl fluoromethyl ether yielded (E) and (Z) fluoromethyl 1,2-difluorovinyl ethers with a trace of fluoromethyl 2,2-difluorovinyl ether.

INTRODUCTION

In previous papers [1,2] we have described the fluorinations, using cobalt (III) fluorides, of ketones, esters, and acid fluorides. We now present some results on the fluorinations of diethyl and ethyl methyl ethers.

There are few reports of reactions of ethers with transition metal fluorides. One of the original descriptions [3] of exhaustive fluorinations by this type of reagent mentioned diphenyl ether as a substrate, the major products being perfluorocyclohexane and perfluorodicyclohexyl ether. More recently [4] the fluorination, with CoF_3, of alkyl perfluorocyclohexenyl ethers to give mixtures of polyfluoroalkyl perfluorocyclohexyl ethers in good yield, has been described. The latter paper also mentions a fluorination of 2-chloro-1,1,2-trifluoroethyl methyl ether to give a low conversion to 2-chloro-1,1,2-trifluoroethyl fluoromethyl ether.

RESULTS AND DISCUSSION

Test fluorinations on a small reactor showed that diethyl ether could be fluorinated with CoF_3 in a very exothermic reaction at 60-80°. Preparative runs gave moderate yields of a mixture of products shown by analytical g.l.c. to contain six major components of which one was very volatile. By a combination of fractional distillation and g.l.c. separation, all six components were isolated pure.

The volatile product was shown by its i.r. spectrum to be 1,2-difluoroethane, it had a quite remarkable ^{19}F n.m.r. spectrum attributable to an AA'XX'X"X''' system, which has been completely analysed [5]. By elemental analysis and mass spectral data the second component was assigned an empirical formula $C_4H_3F_7O$. The ^{19}F n.m.r. spectrum showed the absence of CF_3 groups and was consistent with a structure $CHF_2CHF\ O\ CF_2\ CHF_2$, further indicated by the 'H n.m.r. spectrum (a more detailed discussion of the n.m.r. spectra of this and other ethers is given below). Since this ether contains a chiral centre it exists as a dl mixture but so far no resolution of the enantiomers has been possible.

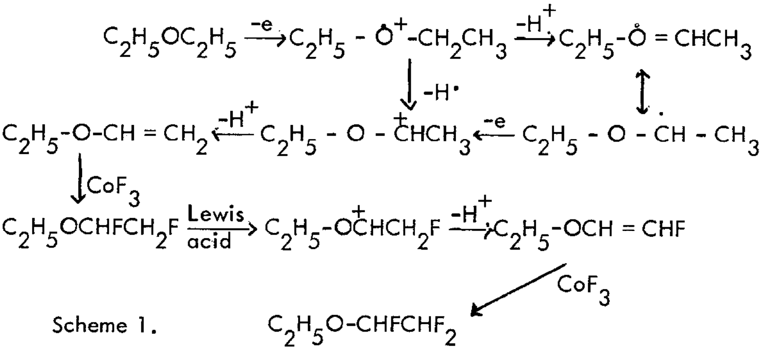
The major component by its analysis and mass spectrum had a formula $C_4H_4F_6O$. The ^{19}F n.m.r. spectra indicated the absence of both CF_3- and CF_2 groups. The data suggested the structure $(CHF_2CHF)_2O$, supported by the 'H n.m.r. data. Since this structure contains two chiral centres, dl and meso forms should be possible. A second stereoisomer was found among the other products, but as yet no evidence is available to decide which configuration each has. Analysis, mass spectrometry, 'H and ^{19}F n.m.r. spectroscopy indicated the general structures $CH_2FCHFOCHFCHF_2$ for the remaining products. Here dl-threo and dl-erythro forms exist, but again it has not been possible to relate each product to a configuration.

In a similar manner, diethyl ether was fluorinated with $KCoF_4$ at 200°. At this temperature, the product, apart from some unchanged ether was largely one component. Analysis and mass spectral data indicated the formula to be $C_4H_7F_3O$ and n.m.r. spectroscopy clearly confirmed the structure as $C_2H_5OCHFCHF_2$ (a trace of this compound was also obtained in the product using CoF_3). If a crude reaction mixture containing this ether was allowed to stand at room temperature, and in some batches even down at -20°, rapid decomposition occurred to give difluoroacetaldehyde diethyl acetal. This has been shown to be due to an acid catalysed hydrolysis. It was shown that storage over calcium carbonate completely stopped the decomposition even at the reflux temperature of the ether, whereas addition of a few drops of concentrated hydrochloric acid to a calcium carbonate treated, vacuum distilled sample rapidly induced decomposition. The major by-product of the decomposition was shown to be difluoroacetaldehyde itself. Finally reflux of the pure ether with ethanol containing a trace of acid gave the acetal with no difluoroacetaldehyde. In contrast the products from the CoF_3 fluorination were all heat stable.

The fluorination of ethyl methyl ether with CoF_3 yielded a mixture containing seven components, four of which were very volatile and could be readily distilled from the bulk mixture. Separation of this volatile fraction by g.l.c. gave, as shown by a comparison of i.r. and n.m.r. spectra with those of authentic samples, 1,1-difluoroethane, 1,1,2-trifluoroethane, 1,2-difluoroethane and 1,1,2,2-tetrafluoroethyl methyl ether, this latter being the product isolated [6] from the reaction of tetrafluoroethylene and methanol. The remaining three compounds were all separated and characterised by elemental analysis, mass spectrometry and n.m.r. spectroscopy. They were dl-1,2,2-trifluoroethyl methyl ether, dl-1,2,2-trifluoroethyl fluoromethyl ether and dl-1,2,2-trifluoroethyl difluoromethyl ether.

It was found that, like ethyl 1,2,2-trifluoroethyl ether, 1,2,2-trifluoroethyl methyl ether was unstable at room temperature but could be stored at -12°. This ether was the sole isolable product from the fluorination of ethyl methyl ether with $KCoF_4$. 1,2,2-Trifluoroethyl fluoromethyl ether was further fluorinated over CoF_3 at higher temperatures. Two major components were isolated from the product mixture 1,2,2-trifluoroethyl difluoromethyl ether and 1,1,2,2-tetrafluoroethyl fluoromethyl ether in about 7:1 ratio.

Nearly all the fluoroethers produced have a CHF_2CHFO-group, and this suggests a fairly specific pattern of fluorination. It is believed [7] that fluorinations by transition metal fluorides may be considered in their initial stages, in terms of oxidation. If we apply this reasoning to fluorinations of ethers by CoF_3 we can in fact rationalise the product formation as shown in Scheme 1.



Scheme 1.

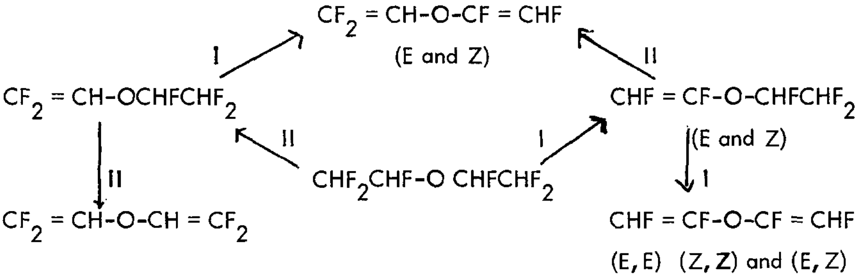
It seems likely that further oxidation of $C_2H_5OCHFCHF_2$ would be more difficult but it would be susceptible to loss of HF perhaps by CoF_3 acting as a Lewis acid and assisting the removal of F from the α carbon (cf the instability of $C_2H_5OCHFCHF_2$ and the known exchanges [8a] of fluorines positioned α to oxygen on cyclic perfluoro ethers). This is further substantiated by the ready interconversions of $(CHF_2CHF)_2O$ isomer A and isomer B over AlF_3 at 260° at which temperature thermal isomerisation does not occur [8b]. Once CHF_2CHF-O-groups have been generated, loss of H from the terminal CHF_2 group would be more difficult (cf the difficulties of dehydrofluorination of R_fCF_2H and of $C_2H_5OCHFCHF_2$ and $(CHF_2CHF)_2O$ (see later)). Repeat of the oxidation process on the other side of the oxygen is however feasible and leads to the predominant products, viz dl and meso bis(1,2,2-trifluoroethyl) ether. The relatively small amount of 1,1,2,2-tetrafluoroethyl 1,2,2-trifluoroethyl ether could arise from further fluorination of the hexafluoro ether possibly in an oxidation fluorination sequence as above via CHF_2-CHF-$O\overset{+}{C}FCHF_2$ as an intermediate which is attacked by F^- to give the observed product.

In the case of fluorinations with $KCoF_4$ it is envisaged that the reaction proceeds as above as far as the 1,2,2-trifluoroethyl ethyl ether stage. As this point, however, $KCoF_4$ could be an insufficiently powerful oxidising agent to form any further radical ions unless forcing conditions (ca 390°) are used.

With ethyl methyl ether it seems that the reaction proceeds readily as far as the trifluoroethyl stage, but subsequent fluorination of the methyl group becomes more difficult even when CoF_3 is used. Probably this is a reflection of the absence of the easiest pathway, elimination of H^+ to the vinyl ether.

In an attempt to confirm that vinyl ethers could be intermediates, we attempted the fluorination of ethyl vinyl ether. Much polymer was formed but some ethers were isolated and the pattern of products was very similar to that found when diethyl ether was fluorinated.

Of particular interest synthetically and mechanistically were the products arising from the dehydrofluorination of the new ethers. The isomers of $(CHF_2CHF)_2O$ could react as shown in Scheme 2.



Mode I elimination involving αH βF

Mode II elimination involving βH αF

Scheme 2.

The major problem that arose was the difficulty of this dehydrofluorination. The ethers could be heated with 18N potassium hydroxide for 24 hours without significant reaction occuring. To achieve any dehydrofluorination it was necessary to pass the vapours of the ether through fused potassium hydroxide at 200-220°. Four products were formed, in similar proportions from each stereoisomer, and were separated and identified by mass spectrometry and n.m.r. spectroscopy. They were (E) and (Z) 1,2,2-trifluoroethyl 1,2-difluorovinyl ether and (Z, Z) and (E, Z) bis(1,2-difluorovinyl) ethers, the identification being based mainly on the value of the olefinic F-F coupling constants. The proportions of each varied slightly with the temperature of the reaction, but in all cases the (Z) isomer was favoured by ca 4:1 and the (Z, Z) by ca 2:1. All the products resulted from Mode 1 eliminations involving αH and βF. The reasons for this exclusive orientation are not obvious. The competing factors in the elimination are (a) the acidities of the hydrogens, (b) the stabilities of the C-F bonds in the $-CHF_2$ and $>CHF$ groups, (c) the stabilities of the product olefins and (d) the effects of the neighbouring groups on the stabilities of the possible transition states.

Of the various elimination processes E_2, E_1 and E_{1cb} it seems possible to discount the latter two. Starting material recovered from the dehydrofluorination of either ether isomer had not isomerised, suggesting that no α carbanion had been formed via an E_{1cb} mechanism. Treatment of either ethers A or B with aluminum fluoride however causes interconversion to a mixture of both forms [8b] presumably via an α carbonium ion, stabilised by the oxygen lone pair, the ion probably existing as part of an ion pair with the tetrafluoroaluminate ion. Thus, an E_1 process should lead to products of eliminations according to Mode II and we are therefore led to the conclusion that the actual reaction is E_2.

An important factor in the eliminations must be the relative acidities of the hydrogen atoms. It is known that the hydrogen in $R_f CHF_2$ is weakly acidic [9] and difficult to eliminate [10]. The effect of the fluoroalkoxy group on the α H is difficult to estimate. Elimination from $(CH_3)_2CHCHBrCH(OEt)_2$ does not lead to the ketene acetal $(CH_3)_2CHCH = C(OEt)_2$, suggesting that ethoxy groups do not play a simple inductive role in the reaction. However, under reaction conditions we have used, 1,2,2-trifluoroethyl methyl- and 1,2,2-trifluoroethyl ethyl ethers do not dehydrofluorinate, suggesting that fluoroalkoxy groups do enhance the acidities of α-H's in some way. Alongside these effects are the stabilities of the C-F bonds present, though those in $-CHF_2$ groups may be less stable than those in $-CF_3$ groups, they are probably mor stable than those in -CHF O- groups. If we consider product stability, it is difficult to choose between $CF_2 = CHOR$ and $CHF = CFOR$ since both have two interactions between fluorine p electrons and double bond electrons and both have an OR- π electron interaction. Thus, the factors controlling the direction of elimination are obscure. Only the hydrogen acidities might be thought to favour Mode I and even this is debatable. It should be emphasised that very forcing conditions are required even to get any elimination to occur.

In the same way that the bis(1,2,2-trifluoroethyl) ethers reacted we found that 1,1,2,2-tetrafluoroethyl 1,2,2-trifluoroethyl ether gave a mixture of (E) and (Z) 1,1,2,2-tetrafluoroethyl 1,2-difluorovinyl ether. It was not found possible to separate the isomers which were indicated to be in the E:Z ratio of 19:81 by ^{19}F n.m.r. spectroscopy. Again Mode I elimination was observed with no evidence for Mode II, even from the CHF_2CF_2O-group, when the hydrogen atom might be thought more acidic than the α H in the CHF_2CHFO-group. Similarly, 1,2,2-trifluoroethyl fluoromethyl ether gave fluoromethyl 1,2-difluorovinyl ether; in this case the (E) and (Z) isomers could be separated by g.l.c. and were in the ratio E:Z 1:5.

In all of these reactions the Z isomers predominated by ca 4.5:1 over the E isomers. Again there is no clear indication why this should be so, based on normal conformation considerations, and the forcing conditions used make detailed speculation useless.

Some simple reactions of the vinyl ethers have been carried out. A mixture of (E) and (Z) 1,1,2,2-tetrafluoroethyl 1,2-difluorovinyl ether and chlorine gave 1,2-dichloro-1,2-difluoroethyl 1,1,2,2-tetrafluoroethyl ether; (Z)-1,2,2-trifluoroethyl 1,2-difluorovinyl ether similarly gave 1,2-dichloro-1,2-difluoroethyl 1,2,2-trifluoroethyl ether, whilst bromine and (Z)-1,2,2-trifluoroethyl 1,2-difluorovinyl ether gave the expected dibromo ether. No resolution of any of the enantiomers formed in these processes has so far been achieved. The reactions of these and other ethers in this series have been further studied [8b] and will be reported later.

The n.m.r. spectra of these ethers proved to be very interesting, but rather complex in some cases. This was particularly so when chiral centres were present on each side of the oxygen atom. In these cases F-F cross oxygen coupling was present and even using computer simulation techniques complete analysis [11] of the spectra was not possible in all cases. In these cases however it was possible to use chemical shift data to determine the gross structure of the ethers e.g. CHF_2CF_2O- could be readily distinguished from CHF_2CHF-O. The vinyl ethers were more amenable to simple analysis and it was possible here to determine the configuration of the double bonds from coupling constant data. The n.m.r. data is summarised in table 1.

Many of the compounds described above are potent anaesthetics and are the subject of current biological testing.

EXPERIMENTAL

Fluorination

Fluorinations were carried out in reactors of conventional design. The products were collected in copper vessels cooled in solid carbon dioxide. At the end of each run the product mixture was warmed to room temperature and washed free of hydrogen fluoride before further processing as described below.

Fluorination of Diethyl ether with CoF_3

In a typical run, ether (150 cm^3) was fluorinated at 60 - 80°. The washed products (85 g) were dried ($CaO/CaCl_2$) to give a mixture shown by g.l.c. analysis to contain six major components. Separation of a portion (4.6 g) of this mixture by preparative g.l.c. by repeated injection using a Pye series 105 machine (Column 9.1 m x 7 mm diisodecylphthalate/chromosorb P 100° N_2 6 l/h) gave (i) four minor components collected together and not identified (0.1 g); (ii) 1,2-difluoroethane (0.08 g) identified by its i.r. [12] and n.m.r. spectra [5]; (iii) 1,1,2,2-tetrafluoroethyl 1,2,2-trifluoroethyl ether nc (0.42 g), b.p. 63° (Found: C, 24.2; H, 1.8; F, 66.1. $C_4H_3F_7O$ requires C, 24.0; H, 1.5; F, 66.5%); (iv) bis(1,2,2-trifluoroethyl) ether (Isomer A) nc (1.69 g), b.p. 85-86° (Found: C, 26.1; H, 2.1; F, 62.5. $C_4H_4F_6O$ requires C, 26.4; H, 2.2; F, 62.6%); (v) 1,2-difluoroethyl 1,2,2-trifluoroethyl ether nc (Isomer A) (0.09 g), b.p. 88° (Found: C, 28.9; H, 3.1; F, 57.7. $C_4H_5F_5O$ requires C, 29.3; H, 3.0; F, 57.9%); (vi) bis(1,2,2-trifluoroethyl) ether nc (Isomer B) (0.84 g), b.p. 94-95° (Found: C, 26.1; H, 2.2; F, 62.4. $C_4H_4F_6O$ requires C, 26.4; H, 2.2; F, 62.6%); (vii) 1,2-difluoroethyl 1,2,2-trifluoroethyl ether nc (Isomer B) (0.06 g) b.p. 98-100° (Found: C, 29.2; H, 3.2; F, 57.8%). A series of fractional distillations was also done on sets of combined products from several such runs at slightly different temperatures to isolate larger samples of the above ethers. The percentages of the products in the mixture were as follows: CH_2FCH_2F 2 - 5; $CHF_2CF_2OCHFCHF_2$ 4 - 14; $(CHF_2CHF)_2O$ (A) 45 - 52; $CHF_2CHFOCHFCH_2F$ (A); 2 - 6 (this was unstable); $(CHF_2CHF)_2O$ (B) 25 - 31; $CHF_2CHFOCHFCH_2F$ (B) 1-3. In addition there was found CHF_2CHF_2 1 - 2 and $CHF_2CHFOC_2H_5$ 1 - 3 (see below).

Fluorination of diethyl ether with $KCoF_4$ (III)

The ether (50 g) was fluorinated over $KCoF_4$ at 200° to yield after work up, a liquid product (50 g), shown by g.l.c. analysis to be essentially two components. Separation of a portion (12 g) by g.l.c. gave (i) diethyl ether (3 g) (ii) ethyl 1,2,2-trifluoroethyl ether nc (5 g), b.p. 52° with decomposition (see later) (Found: C, 37.4; H, 5.2. $C_4H_7F_3O$ requires C, 37.5; H, 5.5%). The residue from this fluorination was allowed to stand at room temperature for three days. The mixture turned black and HF was evolved, g.l.c. analysis revealed the disappearance of ethyl 1,2,2-trifluoroethyl ether and the appearance of a much longer retained compound. Separation of a portion (5 g) of the residue yielded difluoroacetaldehyde diethyl acetal nc (3.0 g) b.p. 96° (Found: C, 46.4; H, 8.0. $C_6H_{12}F_2O_2$ requires C, 46.8; H, 7.8%).

In a subsequent experiment ethyl 1,2,2-trifluoroethyl ether (2 g) was refluxed with ethanol (20 cm^3) and concentrated hydrochloric acid (0.5 cm^3) to yield the above acetal (2.1 g).

In a further experiment, the ether (2 g) was refluxed alone with a few drops of concentrated hydrochloric acid. The volatiles from the reaction were collected in a liquid air cooled trap and the major by-product from this trap was shown by i.r. spectroscopy to be difluoroacetaldehyde.

Fluorination of ethyl vinyl ether with CoF_3

The ether (2 g) was fluorinated at 60° in a small reactor (150 g CoF_3) to yield a product (0.5 g) which showed an identical g.l.c. trace to that obtained from diethyl ether and the peaks of which were all enriched by admixture with a sample of the diethyl ether fluorination mixture.

An attempt to repeat this reaction (150 g scale) yielded only polymeric material and caused explosions within the reactor.

Fluorination of ethyl methyl ether with CoF_3

The ether (75 g) prepared by reaction of sodium ethoxide with methyl iodide was introduced as a gas (5 - 10 l/hr) over 2 hr, into a reactor at 75-100°. Work up as above afforded a clear liquid (71 g) boiling above 19°. The product (175.2 g) from several runs was separated by preparative g.l.c. in six runs (dinonyl phthalate/ chromosorb P 1:5, 4.8 m x 75 mm 90° 65 1 N_2/hr) to give fraction (i) 12.7 g (ii) 48.4 g (iii) 7.2 g (iv) 53.9 g (v) 6.5 g.

Fraction (i) was a mixture of four components which was further separated on the same column as above but at 60° to yield (a) 1,1-difluoroethane (0.1 g) (b) a mixture (7.7 g) further separated using a Pye 105 series machine to yield 1,2-difluoroethane (2.2 g) identified by i.r. spectroscopy and 1,1,2,2-tetrafluoroethyl methyl ether (4.9 g) b.p. 36° (cited [6] 36.4°) identified by its i.r. ^1H and ^{19}F n.m.r. spectra.

Fraction (ii) was a single component shown to be 1,2,2-trifluoroethyl methyl ether nc (48.4g) b.p. 55-57° (Found: C, 31.6; H, 4.1; F, 49.7. $C_3H_5F_3O$ requires C, 31.6; H, 4.4; F, 50.0%).

Fraction (iii) was a mixture (7.2 g) of two components. Separation using a Ucon 50/200 column as above gave (a) 1,2,2-trifluoroethyl methyl ether (0.5 g) (b) 1,2,2-trifluoroethyl difluoromethyl ether nc (3.5 g) b.p. 53° (Found: C, 23.9; H, 2.3; F, 63.1. $C_3H_3F_5O$ requires C, 24.0; H, 2.0; F, 63.3%). Fraction (iv) was a single component 1,2,2-trifluoroethyl fluoromethyl ether nc (53.9 g) b.p. 70-71° (Found: C, 27.6; H, 3.2; F, 58.0. $C_3H_4F_4O$ requires C, 27.3; H, 3.1; F, 57.5%). Fraction (v) was a mixture of at least ten compounds and was not investigated.

Fluorination of 1,2,2-trifluoroethyl fluoromethyl ether

The ether (5.0 g) was fluorinated over CoF_3 at 114° in a small reactor (150 g CoF_3) in a stream of nitrogen (1.5 l/hr) to yield a clear liquid (4.0 g). An aliquot (1.2 g) was separated (10 m Ucon 50/2000 column) to yield (i) 1,1,2,2-tetrafluorethyl fluoromethyl ether (0.09 g) b.p. 51° (cited [13] b.p. 53°) and (ii) 1,2,2-trifluoroethyl difluoromethyl ether (0.67 g) as above.

Fluorination of ethyl methyl ether with $KCoF_4$

The ether (44 g) was fluorinated over $KCoF_4$ at 200° to yield after work up by trap to trap distillation (i) ethyl methyl ether (5.8 g), (ii) a mixture (34.2 g), a portion of which (15 g) afforded on g.l.c. separation (a) ethyl methyl ether (1.7 g) (b) 1,2,2-trifluoroethyl methyl ether (9.3 g) and (c) unidentified minor components (0.22 g).

Dehydrofluorination of bis (1,2,2-trifluoroethyl) ether (Isomer A)

The ether (22.1 g) in ca 5 g portions was passed, in a stream of nitrogen (2 l/hr), through a bath of fused potassium hydroxide (200 g) at 200-220°. The product, (14 g) was washed with iced water (10 cm^3) and distilled by vacuum transfer from P_2O_5. Separation by g.l.c. afforded (i) (E,Z)-bis(1,2-difluorovinyl) ether nc (2.08 g) b.p. ca 38° (Found: M (mass spec.) 142.$C_4H_2F_4O$ requires M 142) (ii) (Z,Z)-bis(1,2-difluorovinyl) ether nc (4.06 g) b.p. ca 42° (Found: M (mass spec.) 142.$C_4H_2F_4O$

requires M 142) (iii) (E)-1,2,2-trifluoroethyl 1,2-difluorovinyl ether nc (0.88 g) b.p. 57-58° (Found: M (mass spec.) 162. $C_4H_3F_5O$ requires M 162) (iv) (Z)-1,2,2-trifluoroethyl 1,2-difluorovinyl ether nc (2.43 g) b.p. 60° (Found: M (mass spec.) 162 $C_4H_3F_5O$ requires M 162). A mixture of (iii) and (iv) above gave on elemental analysis (Found: C, 29.3; H, 1.8; F, 58.5. $C_4H_3F_5O$ requires C, 29.6; H, 1.8; F, 58.6%), (v) unreacted starting material (1.88 g).

In a similar experiment isomer B (20 g) gave the same mixture as above (13 g) in the same proportions.

Dehydrofluorination of 1,1,2,2-tetrafluoroethyl-1,2,2-trifluoroethyl ether

(a) The ether (63 g) was passed through fused potassium hydroxide (200 g) as above to yield a product mixture (36.9 g) shown by analytical g.l.c. to be a mixture of starting material and a shorter retained product. Separation of the mixture by g.l.c. gave (i) 1,1,2,2-tetrafluoroethyl-1,2-difluorovinyl ether nc (15.4 g) b.p. 45-47° (Found: C, 26.8; H, 1.4; F, 63.7. $C_4H_2F_6O$ requires C, 26.7; H, 1.1; F, 63.3%), (ii) starting material (12.2 g).

(b) The ether (3.7 g) was passed in a stream of nitrogen 2 l/hr over a bed of soda lime (123 g) (5-10 mesh) at 150-160°. The product (1.9 g) showed two peaks on analytical g.l.c., separation of a portion (1.1 g) gave (i) the vinyl ether (0.5 g) (ii) starting material (0.3 g).

Dehydrofluorination of 1,2,2-trifluoroethyl fluoromethyl ether

The ether (6.0 g) was passed through fused potassium hydroxide as above at 240-260°. An aliquot (1.2 g) of the total product (4.5 g) was separated by g.l.c. to give (i) fluoromethyl 2,2-difluorovinyl ether nc (0.06 g) b.p. ca 10° (Found: M (mass spec.) 112. $C_3H_3F_3O$ requires M 112). (ii) (E)-fluoromethyl 1,2-difluorovinyl ether nc (0.06 g) b.p. ca 38° (Found: M (mass spec.) 112. $C_3H_3F_3O$ requires M 112). (iii) (Z)-fluoromethyl 1,2-difluorovinyl ether nc (0.31 g) b.p. 45-47° (Found: C, 31.9; H, 2.9; F, 50.9; M 112. $C_3H_3F_3O$ requires C, 32.2; H, 2.7; F, 50.9%, M 112). (iv) Starting material (0.4 g).

Preparation of 1,2-dichloro-1,2-difluoroethyl 1,1,2,2-tetrafluoroethyl ether

1,1,2,2-Tetrafluoroethyl 1,2-difluorovinyl ether (E : Z, 1 : 4) (0.9 g) and chlorine (0.6 g) were sealed in a Carius tube and allowed to stand for 12 hr at 20°. The contents of the tube were then washed with water and distilled in vacuo to give 1,2-dichloro-1,2-difluoroethyl 1,1,2,2-tetrafluoroethyl ether nc (1 g) b.p. 94-95° (Found: C, 19.5; H. 1.0; Cl, 28.2; F, 45.8. $C_4H_2Cl_2F_6O$ requires C, 19.1; H, 0.8; Cl, 28.3; F, 45.4%).

1,2-Dichloro-1,2-difluoroethyl 1,2,2-trifluoroethyl ether

In the same way as just described (Z)-1,2,2-trifluoroethyl 1,2-difluorovinyl ether (0.8 g) yielded 1,2-dichloro-1,2-difluoroethyl 1,2,2-trifluoroethyl ether nc (0.9 g) b.p. 123° (Found: C, 20.8; H, 1.5; Cl, 30.6; F, 40.8. $C_4H_3Cl_2F_5O$ requires C, 20.6; H, 1.3; Cl, 30.4; F, 40.8%).

1,2-Dibromo-1,2-difluoroethyl 1,2,2-trifluoroethyl ether

(Z)-1,2,2-Trifluoroethyl-1,2-difluorovinyl ether (0.8 g) and bromine (1.3 g) were heated together in a sealed Carius tube at 70° for 26 hr. After working up as above distillation in vacuo afforded 1,2-dibromo-1,2-difluoroethyl 1,2,2-trifluoroethyl ether nc (1.4 g) (Found: C, 15.2; H, 0.8; Br, 50.0. $C_4H_3Br_2F_5O$ requires C, 14.9; H, 0.94; Br, 49.7%). This ether decomposes at its boiling point.

TABLE I

^{1}H and ^{19}F n.m.r. data

Compound	^{19}F ppm (rel CCl_3F)	^{1}H	Coupling Constants (Hz)
$(CHF_2CHF)_2O$ Isomer A 1 23 45	135.8(2) 137(3) 150.2(5)	4.04 (1) 4.12 (4)	
$(CHF_2CHF)_2O$ Isomer B 1 23 45	127.9 (2) 129.2 (3) 134.7 (5)	4.0 (1) 4.05 (4)	
$CHF_2CF_2OCHFCHF_2$ 1 2 3 45 67	92 (3) 135 (7) 137 (2) 144 (5)	4.1 (4) 4.2 (1) 4.3 (6)	
$CHF_2CHFOCHFCH_2F$ (A) 1 2 34 56 7 8	136.3 (2) 144.1 (4) 151.9 (6) 243.9 (8)	4.27 (5) 4.34 (1) 4.45 (3) 5.55 (7)	
$CHF_2CHFOCHFCH_2F$ (B) 1 2 34 56 78		4.25 (5) 4.3 (1) 4.45 (3) 5.3 (8)	
$CH_3CH_2OCHFCH_2F$ 1 2 34 56	133 (6) 140 (4)	4.5 (5) 4.8 (3) 6.2 (2) 8.8 (1)	J_{56} 55 J_{34} 55 J_{12} 7.5 J_{13} 1.6 J_{35} 8.5 J_{36} 8.1
$CH_3OCHFCHF_2$ 1 23 4 56	134.9 (5) 136.5 (6) 146.7 (3)	4.94 (4) 4.88 (2) 6.4 (1)	J_{34} 3.2 J_{23} 63.1 J_{56} 302.6 $J_{45}=J_{46}$ 54.1 J_{25} 3.8 J_{26} 5.1 J_{24} 3.8
$CH_2FOCHFCHF_2$ 1 23 4 5 678	135.6 (7,8) 149.2 (5) 158 (3)		

Table I. Contd.

$CHF_2OCHFCHF_2$ 123 45 678	84.9, 86.0 (2,3) 134.7 (7,8) 145.3 (5)	3.62 (1) 4.31 (4) 4.34 (6)	J_{12} 71 J_{13} 14 J_{45} 48 J_{67} 50
(Z) $CHF{=}CFOCHFCHF_2$ 1 2 3 45 67		3.45 (1) 4.5 (4) 4.6 (6)	
(E) $CHF{=}CFOCHFCHF_2$ 1 2 3 45 67		3.4 (1) 4.5 (4) 4.6 (6)	J_{12} 72 J_{13} 4 J_{45} 55 J_{67} 61 J_{46} 4
(E) $CHF{=}CFOCF_2CHF_2$ 1 2 3 4 56	90 (4) 125.5 (3) 137.5 (6) 187 (2)	3.13 (1) 4.2 (5)	J_{13} 123 J_{14} 6 J_{16} 1 J_{12} 72 J_{34} 6.9 J_{23} 4.2 J_{46} 4.9 J_{45} 3.1 J_{56} 53
(Z) $CHF{=}CFOCF_2CHF_2$ 1 2 3 4 56	90.6 (4) 99.7 (3) 136.9 (6) 177.4 (2)	3.47 (1) 4.22 (5)	J_{23} 22.7 J_{12} 70.6 J_{34} 6.8 J_{36} 1 J_{13} 12.1 J_{46} 4.6 J_{45} 2.7 J_{56} 52.7
(Z, Z) $CHF{=}CFOCF{=}CHF$ 12 3 4 56	107 (3,4) 185 (2,6)	3.5 (1,5)	J_{12} 71.3 J_{23} 20.8 J_{13} 12.7
(E, Z) $CHF{=}CFOCF{=}CHF$ 1 2 3 4 56	105 (3) 132 (4) 187 (2) 193.5 (6)	3.26 (5) 3.44 (1)	J_{23} 22.1 J_{12} 71 J_{13} 12.3 J_{34} 4 J_{46} 12.3 J_{45} 4 J_{56} 724
(Z) $CHF{=}CF{-}O\ CH_2F$ 1 2 3 4 5	106.8 (3) 153.8 (5) 187.2 (2)	3.58 (1) 4.62 (4)	J_{23} 16.7 J_{12} 72.1 J_{35} 10 J_{13} 13.5 J_{45} 52.4
(E) $CHF{=}CF{-}O{-}CH_2F$ 1 2 3 4 5	130.5 (3) 150.3 (5) 144.4 (2)	3.31 (1) 4.5 (4)	J_{12} 72.9 J_{13} 3.8 J_{45} 51.9 J_{23} 122.2 J_{35} 6 J_{25} 4.9
$CHF_2CH(OCH_2CH_3)_2$ 12 3 4 5	128 (2)	4.5 (1) 5.8 (3) 6.5 (4) 8.8 (5)	J_{12} 56 J_{13} 4.5 J_{23} 6 J_{45} 7

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