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SYNTHESIS OF PERFLUOROETHERS BY LIQUID PHASE FLUORINATION*

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SUMMARY

Liquid phase fluorination of diethyleneglycol dimethyl ether, tetraethyleneglycol dimethyl ether, 2[1,2-dichloro-1,2-difluoroethyl] tetrahydrofuran and 2[1,2-dichloro-1,2-difluoroethyl] dioxane 1,4 produce the corresponding perfluoroethers in 56, 43, 67 and 74 % yields respectively.

The by-products are partially fluorinated compounds and no fragmentation is observed.

The simplicity of the reactions and method of preparation make this approach to fluorinated fluids and oils industrially attractive.

INTRODUCTION

Saturated perfluoroethers and perfluoropolyethers possess a unique combination of physical and chemical properties making them potentially useful products for industrial applications.

The exceptionally high thermal stability in conjunction with interesting surface properties and low viscosity make these products versatile candidates in numerous applications, e.g. as solvents, inert fluids, lubricants, etc. [1,2].

The first report on the synthesis of perfluoroethers described the electrolysis of hydrogenated ethers in liquid HF [3]. Fluorination of ethers using cobalt trifluoride at 400° C has been studied by Chambers [4], who obtained cyclic perfluoroethers in about 60 % yield, and linear perfluoroethers in roughly 30% yield. However under these conditions not only is the substitution of hydrogen for fluorine observed but also the displacement of chlorine by fluorine.

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

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Direct fluorination has been used to produce perfluorinated ethers by means of the La Mar technique developed by Lagow [5-7] but the reported yields were very low and the reaction times required were very long. The aerosol direct fluorination of cyclic and linear hydrogenated ethers has been studied by Adcock [8,9]. By this technique cyclic perfluorinated ethers have been obtained in about 50 % yields, and linear perfluorinated ethers, such as $CF_3O(CF_2CF_2O)_nCF_3$, in yields which decreased from 36 to 15 % with increasing values of $\underline{n}$ from 1 to 4. Perfluorocyclic ethers have been also prepared by liquid-phase photofluorination using F-hexane and/or 1,1,2-trichloro-1,2,2-trifluoroethane (FC113) as solvent. Neverthless the reported yields were low, about 25-30%, and, if only FC113 was used as reaction medium, concomitant chlorination occurs. Sulfur tetrafluoride has been reported [11] as a fluorinating agent for obtaining fluoroethers from carboxylic acids, carboaldehydes and hydrogenated ethers. However formation of symmetric α-fluoroethers only occurs and perfluoroethers have not been obtained.

All the previously mentioned methods have some limitations, and although some have been adopted on the industrial scale it is clear that a simpler fluorination method would be useful. That is the object of this study.

EXPERIMENTAL

The radical induced addition products of tetrahydrofuran and 1,4-dioxane to 1,2-dichlorodifluoroethene, used as starting materials were prepared as outlined in a previous paper [12]. Perfluoropolyether solvents, Fomblin Y*, were used for these preparations, the glymes were obtained from commercial sources.

Quantitative analysis by GLC were performed on a Carlo Erba gas-chromatrograph Model 4300 equipped with Porapak Q 80-100 mesh. Fluorine NMR spectra were run on a Varian XL-200 spectrometer operating at 188.22 MHz.

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* Fomblin is a Trade Mark of Montefluos SpA.

General procedure for liquid phase fluorination

The apparatus used for liquid phase fluorination is shown in Fig. 1.

A mixture of potassium fluoride and Fomblin was introduced in the reactor, heated to the required temperature and purged with a fluorine-nitrogen flow for 20 mins.

Starting materials were then fed into the reactor at a constant flow rate and the products were collected in a cooled trap. The obtained product contains, beside the perfluorinated ethers, partially fluorinated compounds. These latter products can be recovered by distillation and refluorinated. The reported operating conditions refer to the first fluorination step.

Reaction data are given in Table 1.

Fluorination of $CH_3O(CH_2CH_2O)_2CH_3$

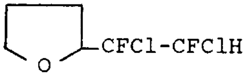
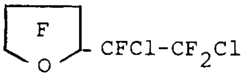
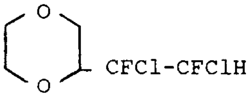
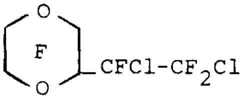
The reactor was charged with 400 g of Fomblin Y04, number average M.W. = 1500, and potassium fluoride (100 g) according to the general procedure outlined above followed by the addition of diglyme (2.16 g) to give 4.6 g of a product. This was subsequently characterized by GLC and ^{19}F NMR spectroscopy and found to contain 76 % of perfluorodiglyme. Spectroscopic properties were in good agreement with ref. 9.

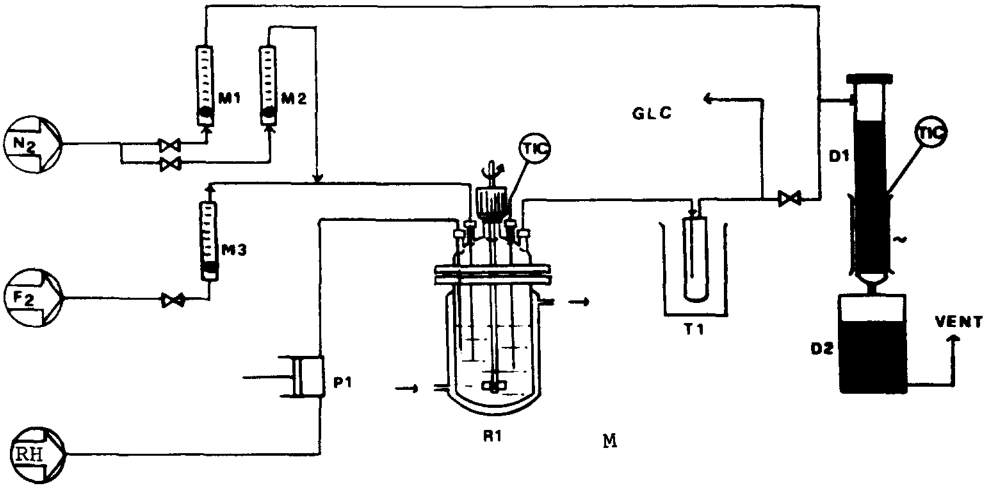
Fluorination of $CH_3O(CH_2CH_2O)_4CH_3$

The reactor was charged with 400 g of Fomblin Y25, M.W. = 2800, and 100 g of potassium fluoride, followed by the addition of tetraglyme (2.3 g) obtaining 3.7 g of product containing 75 % perfluorotetraglyme. The product was characterized by ^{19}F NMR spectroscopy and GLC analysis. Spectroscopic properties were in good agreement with ref. 9.

TABLE 1

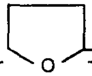
Liquid phase fluorination operating conditions

Starting compound	F_2 flow Nl/h	N_2 flow Nl/h	Ether rate ml/h	Reaction time h	T (°C)	Reaction product
$CH_3O(CH_2CH_2O)_2CH_3$	3	3	0.38	6	100	$CF_3O(CF_2CF_2O)_2CF_3$
$CH_3O(CH_2CH_2O)_4CH_3$	3	3	0.38	6	120	$CF_3O(CF_2CF_2O)_4CF_3$
	3	3	0.95	7	100	
	3	3	0.95	6.5	100	

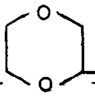


R1	Glass reactor equipped with an electric stirrer
P1	Metering pump
T1	Trap cooled at -80 °C
D1	Fluorine disposal (charcoal 300 °C)
D2	Soda lime
M1,2,3	Flowmeters

Fig. 1. Apparatus for liquid phase fluorination.

Fluorination of  CFCl-CFClH

The reactor was charged with Fomblin Y04 (400 g) and potassium fluoride (100 g) followed by addition of 9.1 g of the titled ether to give 14.8 g of product. GLC analysis and ^{19}F NMR spectroscopy data showed that the product contained 70 % chlorofluoroethers.

Fluorination of  CFCl-CFClH

The reactor was charged with Fomblin Y25 (400 g), potassium fluoride (100 g) followed by the addition of the titled ether (8.8 g), all in accordance with the general procedure.

A product (13.4 g) was obtained whose GLC analysis indicated the chlorofluoroether to be present in 80 %.

This product was also characterized by ^{19}F NMR spectroscopy.

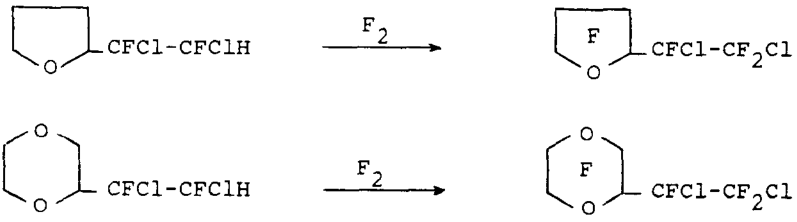
RESULTS AND DISCUSSION

Fluorination of cyclic and linear hydrogenated ethers by elemental fluorine in perfluoropolyether solvent containing an HF scavenger (KF), produces the corresponding fluorinated ethers in improved yields. The intrinsic simplicity of this direct fluorination technique makes this process practical for industrial applications.

While extensive, sometimes violent, fragmentation usually results from direct fluorination procedures, this liquid phase fluorination method takes advantage of effective dissipation of the heat of reaction which significantly decreases fragmentation. The low concentration of fluorine in the system reduces also the likelihood of simultaneous attack by two fluorine molecules or radicals on adjacent sites in a molecule, which would increase the probability of fragmentation.

Hydrogenated ethers require high temperatures for complete fluorination and the fact that the products of reaction can withstand these conditions is, in itself, evidence for the remarkable inertness of these compounds. The technique permits complete fluorination of the starting hydrogenated compounds by recycling the partially fluorinated ether.

In the fluorination of 2[1,2-dichloro-1,2-difluoroethyl] tetrahydrofuran and 2[1,2-dichloro-1,2-difluoroethyl]dioxane-1,4 no substitution of chlorine atoms by fluorine was observed.



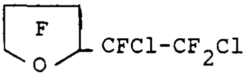
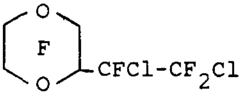
Hence under these reaction conditions, fluorination of chlorohydrogenated compounds produced only the corresponding chlorofluorinated products which are useful intermediates for the synthesis of unsaturated perfluoroethers.

Yields and boiling points of fluoroethers after the first fluorination step are shown in Table 2. Diastereomeric cyclic ethers prepared were not completely separable by distillation.

The structures of fluoroethers were confirmed by fluorine NMR spectroscopy. Cyclic ethers require a 2-dimensional NMR technique to assign the resonance peaks to the various fluorine atoms. The range of their chemical shifts is due to chiral overlap. Details of the NMR data are shown in Table 3.

TABLE 2

Results and physical properties

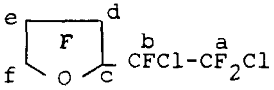
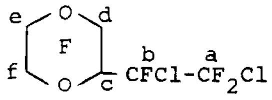
Product	B.p. °C	Yield %
$CF_3O(CF_2CF_2O)_2CF_3$	66	56
$CF_3O(CF_2CF_2O)_4CF_3$	138	43
	108	67
	125	74

CONCLUSIONS

On the basis of the foregoing results it is clear that the fluorination technique reported here affords good yields from a simple, easily scaled method. Additionally it has the distinct advantage of selectively substituting fluorine for hydrogen in the presence of certain chlorine substituents.

TABLE 3

^{19}F NMR data for fluoroethers

Compound	Chemical shift (δ $CFCl_3$)	
$\overset{a}{CF_3}O\overset{b}{CF_2}\overset{c}{CF_2}OCF_2CF_2OCF_3$	$CF_3{}^a$	55
	$CF_2{}^b$	90
	$CF_2{}^c$	88
$\overset{a}{CF_3}O\overset{b}{CF_2}\overset{c}{CF_2}O(CF_2CF_2O)_3CF_3$	$CF_3{}^a$	60
	$CF_2{}^b$	105
	$CF_2{}^c$	103
	$CF_2{}^a$	60 - 65
	CF^b	114 - 120
	CF^c $CF_2{}^d$	125 - 130
	$CF_2{}^e$	125 - 138
	$CF_2{}^f$	80 - 90
	$CF_2{}^a$	64 - 68
	$CF^{b,c}$	126 - 136
	$CF_2{}^{d,e,f}$	80 - 98

REFERENCES

1 R.Banks, 'Preparation, properties and industrial applications of organofluorine compounds', Ellis Horwood, Chichester, p. 28.

2 G.Caporiccio, J. Fluorine Chem., 34, 314 (1986).

3 J.Burdon, J.C. Tatlow, Advances in fluorine chem., 1, 129, Butterworths, London, 1965.

4 R.D.Chambers, B.Grievson, J. Fluorine Chem., 29, 323 (1985).

5 R.J.Lagow, J.L.Margrave, Prog. Inorg. Chem., 26, 161 (1979).

6 W.H.Lin, W.I.Bailey, Jr. and R.J.Lagow, J. Chem. Soc. Chem. Comm., (1985) 1350.

7 D.F.Persico,G.E.Gerhard,R.J.Lagow, J. Am. Chem. Soc., 107, 1197 (1985).

8 J.L.Adcock, K.Horita, E.B.Renk, J. Am. Chem. Soc. 103, 6937 (1981).

9 J.L.Adcock, M.L.Cherry, J. Fluorine Chem., 30, 343 (1985).

10 K.Sherer, Eur. Pat. 190 393 (1986).

11 W.Dmowski, J. Fluorine Chem., 32, 255 (1986).

12 S.Modena, A.Fontana, G.Moggi, J. Fluorine Chem., 30, 109 (1985).