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PRELIMINARY NOTE

A New Route to Perfluorinated Ethers

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SUMMARY

Partly fluorinated ethers, obtained by free-radical addition of ethers to perfluorinated-alkenes or -cycloalkenes, are converted to perfluoroethers, using cobalt trifluoride at very high temperatures.

Perfluorinated ethers and related compounds are potentially very important for use as inert fluids in various applications [1] but synthesis of such compounds has previously involved either electrochemical fluorination [2] or small-scale sophisticated methods of direct fluorination [3]. Consequently, this class of compounds has remained relatively inaccessible and, here, we report a simple laboratory method that is applicable to the synthesis of a wide range of perfluorinated ethers. It is well known [4] that cobalt trifluoride and related systems may be used to replace, extensively, hydrogen in many organic compounds by fluorine but previous publications on the reactions of ethers with this reagent have described complicated products, including extensive fragmentation, with only low yields of corresponding perfluoroethers [5].

Free-radical additions of ethers to perfluorinated-alkenes and -cycloalkenes have been demonstrated by other workers [6] and in more recent work we have shown that a variety of partly fluorinated ethers may be obtained from such reactions depending on the ether and fluorinated alkene used [7].

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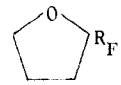
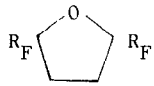
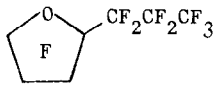
E.g.  + $CF_2{=}CFCF_3$ $\xrightarrow{(i)}$  + 

(1) (2)

(i) $(t\text{-}BuO)_2$, 120°C or γ-Rays, R.T. ($R_F = CF_2CFHCF_3$)

In the course of investigating the chemistry of these adducts e.g. (1) and (2), we have now found that many of these partly fluorinated ethers are remarkably robust during fluorinations with cobalt trifluoride. Complex mixtures are obtained at lower temperatures but these simplify as the temperature is raised and our remarkable finding is that, at very high temperatures, perfluoroethers may be obtained in high yield and purity. For example, reaction of adduct (1), with cobalt trifluoride at 440°C (in a single pass over a stirred bed) gave perfluoro-2-propyloxolane (3) in 70% isolated yield. Compound (3) was easily identified by ^{19}F n.m.r. and has previously been obtained by electrochemical fluorination [8].

(1) $\xrightarrow{(ii)}$  (70%)

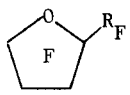
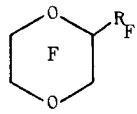
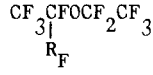
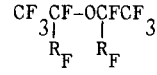
(3)

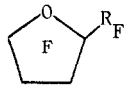
(ii) CoF_3, stirred bed, N_2 flow, 440°C

Remarkably, for such a high reaction temperature, the product showed a single component containing only a trace amount of perfluoro-n-hexane, which is easily separated by distillation.

TABLE

Perfluorinated ethers obtained by fluorination of partly fluorinated ethers (% yields)

				
$R_F = CF_2CF_2CF_3$	70%	68%	43%	41%

 $R_F = CF(CF_3)CF_2CF_3$, = 

53% 64%

Snown facing are some of the range of perfluorinated ethers that have now been made using this simple approach of free-radical addition of an ether to a perfluorinated-alkene or -cycloalkene, followed by reaction with cobalt trifluoride at very high temperatures. New compounds have been fully characterised by elemental analysis, mass spectrometry, and ^{19}F n.m.r. spectroscopy; percentage yields are shown in the Table.

The reasons for the dramatic effect of perfluoroalkyl groups on the stability towards further fluorination are not yet clear but further work is proceeding in this area.

1 D.S.L. Slinn and S.W. Green, Chapter 2 in 'Preparation, Properties and Industrial Applications of Organofluorine Compounds', Ed. R.E. Banks, Ellis Horwood, Chichester, 1982.

2 See for example T. Abe and S. Nagase, Chapter 1, ref. 1, and references contained.

3 R.J. Lagow and J.L. Margrave, Progress in Inorg. Chem., 26 (1979) 161.

4 R.D. Chambers, 'Fluorine in Organic Chemistry', Wiley-Interscience, p.25.

5 M. Brandwood, P.L. Coe, C.S. Ely and J.C. Tatlow, J. Fluorine Chem., 5 (1975) 521; J. Burdon, G.E. Chivers, E.F. Mooney and J.C. Tatlow, J. Chem. Soc. C, (1969) 1739 and references contained.

6 See for example H. Muramatsu, K. Inukai and T. Ueda, Bull. Chem. Soc. Jap., 40 (1967) 903.

7 R.D. Chambers, B. Grievson and N.M. Kelly, forthcoming publications.

8 I.P. Kolenko, N.A. Ryabinin and B.N. Lundin, Tr. Inst. Khim. Akad. Nauk SSSR, Ural Filial., 15 (1968) 59; Chem. Abs., 70 (1969) 87422f.