Synthesis of Perfluoropoly(ethylene glycol) Ethers: $CF_3-[O-CF_2-CF_2]_n-O-R_f$ ($R_f = CF_3$ or C_2F_5; $n = 1-5$)

By GLENN E. GERHARDT and RICHARD J. LAGOW*
(*Department of Chemistry, University of Texas at Austin, Austin, Texas* 78712)

Summary A new synthetic method for the preparation of high molecular weight fluorocarbon ethers has been developed; polyethylene oxide was caused to react with elemental fluorine under conditions carefully regulated to fragment and perfluorinate the polyether system and yield a number of new fluorocarbon ethers.

PERFLUOROETHERS are of considerable current interest for use as high-stability fluids, lubricants, and greases and for their potential as fluorocarbon solvents. Their synthesis, however, is difficult using the existing techniques. By use of the LaMar[1] direct fluorination technique, the ten title compounds, perfluoromono-, di-, tri-, tetra-, and pentaglyme (ethylene glycol dimethyl ether) and perfluoromono-, TABLE. Properties and proportions of compounds (**1a**—**e**) and (**2a**—**e**) in volatile product mixture. ^{19}F n.m.r. shifts are in p.p.m. *vs.* 1% aq. ext. CF_3CO_2H, with relative intensities in parentheses for the c resonances.

			Mole % in prod.	^{19}F n.m.r. data				
Compound	M.p./°C	B.p./°C	mixt.	F^a(t)†	F^b(q)‡	F^c(s)	F^d(s)†	J_{ab}/Hz
(**1a**)	—	—	14·6	−16·3	18·3	—	—	10
(**2a**)	—	—	7·6	−16·3	18·2	16·2 (4)	15·0	10
(**1b**)	—	66—66·5	8·7	−16·4	18·2	16·1 (2)	—	9
(**2b**	—	81·5—82	4·9	−16·6	18·0	16·0 (8)	14·8	9
(**1c**)	−82 to −80·5	104·5—105	8·1	−16·6	18·1	16·0 (4)	—	9
(**2c**)	−80 to −78	117·5—118·5	5·7	−16·7	18·0	15·9 (12)	14·7	9s
(**1d**)	−71 to −69·5	138—138·5	6·8	−16·6	18·0	15·9 (6)	—	9
(**2d**)	−60·5 to −60	146·5—148	5·3	−16·8	17·8	15·8(16)	14·6	10
(**1e**)	−47 to −46	164—164·5	5·9	−16·8	17·8	15·8 (8)	—	10
(**2e**)	−47 to −46	173·5—174	4·3	−16·7	17·9	15·8 (20)	14·6	10

s = singlet; t = triplet; q = quartet.
† Relative intensity 3. ‡ Relative intensity 2.

di-, tri-, tetra-, and penta-ethylene glycol methyl ethyl ether, have been produced. Of these ten compounds only three, perfluoroglyme[2,3,4] perfluorodiglyme,[3] and perfluoroethylene glycol methyl ethyl ether,[4] have been reported previously.

Finely ground (<120 mesh) poly(ethylene oxide) polymer can be caused to react with elemental fluorine to produce an extremely stable high-molecular weight perfluoropolyether;[5] however, conditions were chosen in this study to promote polymer fragmentation. The initial fluorination conditions were 40 $cm^3 min^{-1}$ He and 1·0 $cm^3 min^{-1}$ F_2 at ambient temperature. As the reaction progressed, the temperature remained constant while the gas-flow rates were adjusted in a step-wise manner until flow rates of 10 $cm^3 min^{-1}$ He and 4·0 $cm^3 min^{-1}$ F_2 were reached. At that point, the gas-flow rates were held constant while the temperature was raised in a step-wise manner to 110 °C. The time of reaction at each set of conditions was determined by trial and error, and the total reaction time was proportional to the amount of starting material used.

The volatile products, trapped at −196 °C throughout the reaction, were fractionated on a vacuum line. Pure compounds were isolated by g.l.c. assay of the fractions and were identified by spectroscopic analysis. In a typical reaction, 40 g of starting material yielded 9 g of volatile perfluoroether products. The composition of the product mixture along with the m.p.'s and b.p.'s of the compounds are shown in the Table.

The gaseous i.r. spectra of all compounds were very similar in showing strong, broad absorptions between 1125 and 1300 cm^{-1} (C–F stretch and C–O stretch) and several weaker and sharper bands below 1000 cm^{-1}.

The mass spectra were recorded with the ion source of the mass spectrometer cooled to room temperature in order to lessen chain fragmentation and rearrangement. For each compound, the highest mass peak observed in the room temperature mass spectrum is the parent minus fluorine peaks, *i.e.*: for $C_4F_{10}O_2$, 251 ($C_4F_9O_2^+$); for $C_5F_{12}O_2$, 301; for $C_6F_{14}O_3$, 367; for $C_7F_{16}O_3$, 417; for $C_8F_{18}O_4$, 483; for $C_9F_{20}O_4$, 533; for $C_{10}F_{22}O_5$, 599; for $C_{11}F_{24}O_5$, 649; for $C_{12}F_{26}O_6$, 715; and for $C_{13}F_{28}O_6$, 765. By far the most intense peaks of the room temperature spectra were *m/e* 69 (CF_3^+) and 119 ($C_2F_5^+$) with peak intensity decreasing with mass, a characteristic common to many fluorocarbons.[6]

The ^{19}F n.m.r. spectra were extremely useful in compound identification. Each dimethyl ether compound exhibited (average values for all the compounds are given here for shifts and coupling constants) a triplet at −16·5 p.p.m. and a quartet at +18·0 p.p.m. with a coupling constant of 9·5 Hz and a singlet at +16·0 p.p.m. relative to 1% aq. CF_3CO_2H (external). Each methyl ethyl ether compound exhibited the same peaks as the dimethyl ether compounds and an additional singlet at +14·7 p.p.m. The signal assignments are shown below, and the ^{19}F n.m.r. data are shown in the Table.

$$CF^{a}_{3}OCF^{b}_{2}[CF^{c}_{2}OCF^{c}_{2}]_{x}CF^{b}_{2}OCF^{a}_{2}$$

(**1**)

$$CF^{a}_{3}OCF^{b}_{3}[CF^{c}_{2}OCF^{c}_{2}]_{x}CF^{c}_{2}OCF^{c}_{2}CF^{d}_{3}$$

(**2**)

a; $x = 0$
b; $x = 1$
c; $x = 2$
d; $x = 3$
e; $x = 4$

For all compounds, the experimental relative intensities of the signals correspond exactly to the calculated relative intensities. No signals were observed for any of the compounds in ^1H n.m.r. scans.

We are grateful for support from the Air Force Office of Scientific Research for this work.

(*Received*, 25th *November* 1976; *Com.* 1306.)

---

[1] R. J. Lagow and J. L. Margrave, *Proc. Nat. Acad. Sci. U.S.A.*, 1970, **67**, 4, 8A.
[2] J. H. Simons, U.S.P. 2,500,388 (1950).
[3] J. L. Adcock and R. J. Lagow, *J. Org. Chem.*, 1973, **38**, 3617.
[4] V. V. Berenblit, Yu. P. Dolnakov, V. P. Sass, L. N. Senyushov, and S. V. Sokolov, *Zhur. org. Khim.*, 1974, **10**, 2031.
[5] R. J. Lagow and S. Inoue, U.S.P. appl. No. 597,937.
[6] 'Advances in Fluorine Chemistry,' Eds. M. Stacey, J. C. Tatlow, and A. G. Sharpe, Vol. 2, Butterworths, Washington, 1961, pp. 55—103.