The First Perfluoro Crown Ethers

Wen-Huey Lin, Webb I. Bailey, Jr., and Richard J. Lagow*

Department of Chemistry, The University of Texas, Austin, Texas 78712, U.S.A.

The first perfluoro crown ethers, perfluoro 18-crown-6, perfluoro 15-crown-5, and perfluoro 12-crown-4, have been prepared by carefully controlled elemental fluorination; although they are weaker bases than their parent compounds, perfluoro crown ethers are materials which will have a number of applications.

Perfluoro crown ethers have been synthetically inaccessible by conventional reactions of fluorocarbons and outside the capabilities of synthesis by fluorination using selective fluorination reagents. Examples of this potentially useful class of macrocycles have been prepared recently in our laboratory. These syntheses have been accomplished using the broadly applicable techniques for controlling reactions of elemental fluorine (LaMar) developed in our laboratory and the reactions were conducted in the previously described cryogenic fluorination reactor.[1]

Perfluoro crown ethers are expected to be unusually stable. The reactions to produce perfluoro 18-crown-6, perfluoro

Table 1. Fluorination parameters for 18-crown-6.

Time (h)	He (cm^3 min^{-1})	F_2 (cm^3 min^{-1})	Temp. (°c)
16	60	0	−78
23	40	1.0	−78
24	20	1.0	−78
24	10	1.0	−78
24	10	3.0	−78
24	0	1.0	−78
36	0	2.0	−78
29	0	2.0	Room temp.
24	0	2.0	45
47	0	2.0	60
24	60	0	60
295			

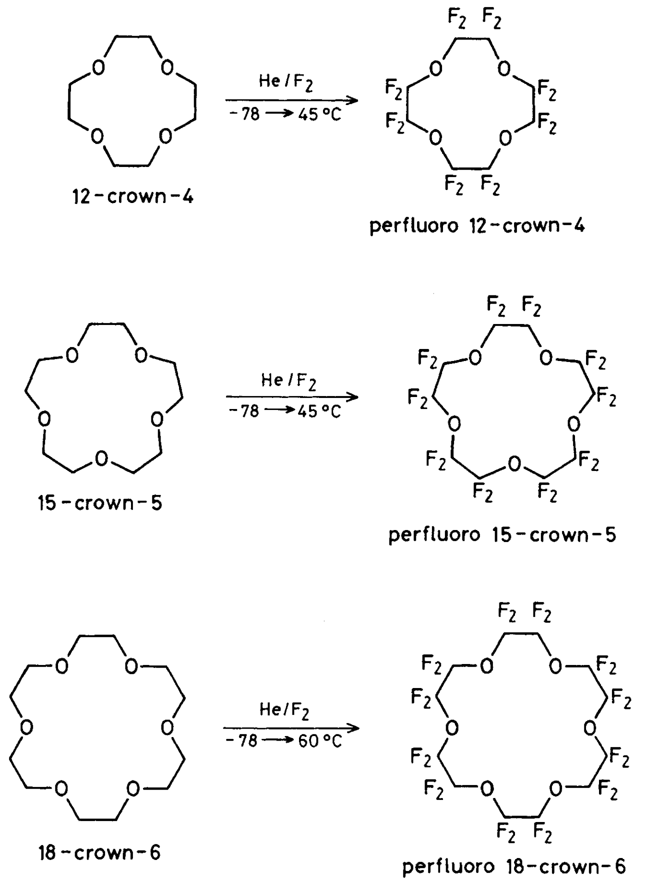
Table 2. Fluorination parameters for 15-crown-5 and 12-crown-4.

15-crown-5:

Time (h)	He (cm^3 min^{-1})	F_2 (cm^3 min^{-1})	Temp. (°C)
18	60	0	−78
25	40	1.0	−78
24	20	1.0	−78
24	10	1.0	−78
29	10	3.0	−78
40	0	1.0	−78
43	0	2.0	−78
29	0	2.0	Room temp.
24	0	2.0	45
24	60	0	45
280			

12-crown-4:

Time (h)	He (cm^3 min^{-1})	F_2 (cm^3 min^{-1})	Temp. (°C)
20	60	0	−78
22	40	1.0	−78
25	20	1.0	−78
24	10	1.0	−78
24	10	3.0	−78
33	0	1.0	−78
37	0	2.0	−78
24	0	2.0	Room temp.
27	0	2.0	45
24	60	0	45
260			



Scheme 1

Table 3. Properties and characterization of perfluoro 15-crown-5 and perfluoro 12-crown-4.[a] Satisfactory elemental analyses (C, F) were obtained.

	15-crown-5	12-crown-4
Boiling point, °C	146	118
I.r. (vapour phase), cm^{-1}	1250(s), 1228(vs), 1158(vs), 745(m)	1260(vs), 1188(vs), 1160(vs), 1080(m), 825(m), 745(br)
N.m.r. (neat liquid)	^{19}F −91.8(s) p.p.m. (ext. $CFCl_3$) ^{13}C δ 114.9 (s)	^{19}F −90.0(s) p.p.m. (ext. $CFCl_3$) ^{13}C δ 114.9 (s)
Mass spectrum, *m/z*	580 ($C_{10}F_{20}O_5$, M^+)	445 ($C_8F_{15}O_4$, $M^+ - F$)

[a] A table for the straight-chain fragmentation products listing mass spectral and ^{19}F data (two pages) is available from the authors.

15-crown-5, and perfluoro 12-crown-4 are illustrated in Scheme 1.

The starting hydrocarbon crown ether was purified by distillation and recrystallization. In a typical experiment, 18-crown-6 (0.81 g) and NaF (2.09 g) were ground to a fine powder and mixed well in a dry-box. We found for these experiments that several factors influenced the yields obtained: the surface area exposed to fluorine, the reaction temperatures, the reaction time, and the fluorination conditions. The surface area variable was particularly important. To increase the surface area, sodium fluoride was used as a solid support upon which the starting crown ether was coated. A second function of this sodium fluoride was to react with the hydrogen fluoride produced as the reaction proceeds.

The mixture was placed in a nickel boat and loaded into a fluorination reactor. A trap was attached to the reactor and used to collect the volatile products. After a He purge of several hours, the reactor and trap were cooled to −78 °C. The fluorination reaction was started and followed the conditions shown in Table 1. After the reaction. He was passed through the reactor to sweep F_2 from the system.

The volatile products produced were transferred from the −78 °C trap to a vacuum line for fractionation. Fractions that stopped at −23 and −78 °C were further separated using a gas chromatograph with a fluorosilicone column.

The major component was identified as perfluoro 18-crown-

6. Perfluoro 18-crown-6 was a volatile colourless crystalline solid, m.p. 34 °C, obtained in 33.5% yield (0.715 g based on starting 18-crown-6) which could be easily sublimed. The elemental analyses were consistent with $C_{12}F_{24}O_6$. The vapour phase i.r. spectrum exhibited bands at 1240(vs), 1220(vs), 1140(vs), and 730(m) cm^{-1}. The ^{19}F n.m.r. spectrum (C_6F_6 solution) contained a singlet at −91.0 p.p.m. from external $CFCl_3$. The ^{13}C n.m.r. spectrum (C_6F_6 solution) also contained a singlet which was observed at δ 114.9. The mass spectrum (with the spectrometer cooled to ambient temperature) gave no parent peak but a signal at *m/z* 677 was observed which corresponded to the molecular ion minus one fluorine. The remaining two fractions from the g.c. separation were identified as $CF_3O(CF_2CF_2O)_4CF_3$ (40 mg) and $CF_3CF_2O(CF_2CF_2O)_4CF_3$ (22 mg). These reaction by-products resulted from the fragmentation of the ring system to produce the straight-chain perfluoro polyethers.

The preparations of 15-crown-5 and 12-crown-4 were performed in a similar manner. The fluorination parameters used are listed in Table 2. The properties and characterization of perfluoro 15-crown-5 and perfluoro 12-crown-4 are listed in Table 3.

Perfluorinated derivatives of hydrocarbon compounds usually exhibit different properties than their hydrocarbon analogues. The perfluoro crown ethers are markedly more volatile than the hydrocarbon products. One would expect the dimensions of the pocket size to change. A decrease in the basicity of the crown ether would also be predicted and a key question is whether the perfluoro crown ethers can co-ordinate metals and organometallic species. This interaction, which is expected to be much weaker, is under study. Single crystals have been grown of 18-crown-6 and preliminary structural information indicates that the ring is puckered in a manner so that oxygen is exposed and projected toward a metal co-ordination site.[2] In addition to the possibility of serving normal functions as macrocyclic ligands, the compounds are of interest in the biomedical and oxygen carrier areas for they are definitely physiologically compatible with human and other mammalian tissue.[3]

This synthetic breakthough opens the possibility of preparation of many novel crown ether systems as well as the synthesis of perfluoro cryptands. Such ligands should be much less subject to chemical attack or thermal degradation.

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

Received, 10th May 1985; Com. 639

References

1 J. L. Margrave and R. J. Lagow, *Prog. Inorg. Chem.*, 1979, **26**, 161.
2 S. H. Simonsen, S. B. Larson, W. H. Lin, W. I. Bailey, Jr., and R. J. Lagow, *J. Am. Chem. Soc.*, in the press.
3 R. J. Lagow, W. H. Lin, and L. C. Clark, unpublished work.