ELECTROCHEMICAL FLUORINATION OF AMINOALKYL ETHERS

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SUMMARY

It is known that the electrochemical fluorination of trialkylamines in liquid HF takes place readily in good yields, whereas dialkyl ethers give low yields. The latter fluorinated ethers are of interest for their low temperature properties. Our goal in this work was to prepare fluorinated aminoalkyl ether fluids which might combine the favorable yields of amines and properties of ethers. Several dialkylamine and alkylene units were combined in a variety of diamino monoethers, diamino diethers, and monoamino monoethers. Electrochemical fluorination yields as high as 50% were obtained in materials of the first class. The structure-yield relationships and the properties of these new fluids are described.

INTRODUCTION

This study is part of our long-term effort to define useful structure-yield relationships in electrochemical fluorination (ECF) of organic compounds dissolved in liquid HF (Simons ECF). Simons ECF is a high energy process in which perfluorination (replacement of C-H by C-F) is often accompanied by considerable side reactions [1,2,3]. Yields in practice are limited especially by poor conductivity (often but not always associated with resinous products - "tars" - on the anode), by cleavage of C-C and C-heteroatom bonds, with formation of lower molecular weight products or apparent recombination to isomeric or higher

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molecular weight products, and by retention of small amounts of hydrogen.

Previous workers have shown that these problems cause decreasing yields with increasing carbon chain length in the commercially important chemical classes, e.g. R_3N, RSO_2F, RCOF, and are dominant in some classes, e.g. ethers. Our long-range goal is to find the organic structural features that minimize these side reactions and thus maximize the yields, making new products commercially feasible.

The shorter range focus of this work was extension of the liquid range of ECF-derived perfluorinated inert fluids. We desired materials in the current boiling ranges (to 260°C) having lower pour points and materials with higher boiling points. Acyclic perfluoroethers are known to have low-temperature fluidity superior to that of other perfluorinated materials, but generally ECF of higher ethers gives tarring and cleavage. We decided to modify the ethers by introducing amino groups, in hopes of introducing the good conductivity and yields of trialkylamines while retaining the low pour points of ethers. Benninger and co-workers have described a similar rationale for their ECF synthesis of acyclic perfluoroaminoethers [4]. Their approach was made possible by the higher yields obtainable by ECF of partially fluorinated ethers, in this case the adducts of fluoroolefins and aminoethanols. This led to structures in which a central nitrogen atom was flanked by one or more F-alkoxyethyl groups, e.g., $(C_4H_9)_2NCH_2CH_2OCF_2CFHCF_3$ and $C_4H_9N(CH_2CH(CH_3)OCF_2CF_2H)_2$. A disadvantage of this synthetic route lies in the relatively high cost of these starting materials, especially since the ECF yields of distilled products were only moderate (in the above examples, 34 and 15%, respectively.)

RESULTS AND DISCUSSION

Our approach placed the oxygen in the center, flanked by two dialkylaminoalkyl groups (R_2N-alkylene-O-alkylene-NR_2), in order to make maximal use of the flexibility associated with the oxygen atom. This use of three heteroatoms also breaks up the longer carbon chains into short, more flexible units. However, this

approach requires discovery of units that fluorinate without cleavage. Benninger et al. indicate that the hydrocarbon analogs of their partially fluorinated aminoethers gave little or no perfluorinated aminoethers [4].

We thus initially avoided the aminoethyl ethers, presuming them to be relatively unstable to ECF cleavage. We instead evaluated a series of aminobutyl and aminophenyl ethers (Table 1). The first compound tested (1) gave an encouraging yield of material boiling in the expected range and which proved to be primarily the expected fluorinated structure. However, ECF yields on the remainder of the compounds in Table 1 were not as good. We then turned to the ECF of aminoethyl ethers and surprisingly obtained high yields of symmetrical (Table 2), asymmetrical (Table 3), and methylated derivatives (Table 4). Application of these findings to diethers gave lower, but potentially useful yields (Table 5). However, extension to monoamines was unsuccessful (Table 6).

Organic synthesis

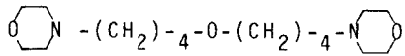
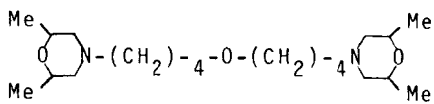
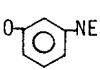
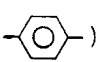
The hydrocarbon precursors, R_2N-alk-O-alk'-NR'_2, are listed in Table 7 in the order in which they appear in Tables 1-6 and were prepared by two general methods (A and B).

A. Phase transfer catalysed Williamson ether synthesis

The quaternary ammonium salt-catalysed method of Freedman and Dubois was found to be very effective in coupling $R_2NCH_2CH_2Cl$ with alkoxides [5]. Less reactive alkyl chlorides such as $C_6H_{13}Cl$ and $R_2NCH_2CH_2CH_2Cl$ gave poorer yields. The reactions of $R_2NCH_2CH_2Cl$ with $R'_2NCH_2CH_2OH$ and $R'NCH_2CH(CH_3)OH$ (to asymmetrical ethers) were complicated by reaction of the chloride with hydroxide to give $R_2NCH_2CH_2OH$ and thence the symmetrical ether, $R_2NCH_2CH_2$-O-$CH_2CH_2NR_2$, as by-product. An additional complication appeared in reactions of the aminoisopropyl chlorides. The major products from these proved the beta methylethyl ethers, indicating formation of the aziridinium ion and alkoxide attack at the less hindered carbon. The reaction of $R_2NCH_2CH(CH_3)Cl$ with $HOCH(CH_3)CH_2NR'_2$ was even more complex, with the major alpha, beta dimethyl ether being accompanied by the beta,

TABLE 1

Initial ECF

		Yield	BP [a]	pp [b]
1. 	C_{16}	23%	200-35°	(0° solid)
2. $Et_2N-(CH_2)_4-O-(CH_2)_4NEt_2$	C_{16}	19%	200-210°	-
3. $Pr_2N-(CH_2)_4-O-(CH_2)_4NPr_2$	C_{20}	7%	240-60°	-
4. 	C_{20}	10%	240-65°	-
5. $Et_2NCH_2CH_2O$  NEt_2	C_{16}	18%	210-25°	-40°
6. $(Et_2N$  $)O$	C_{20}	7%	220-60°	-30°

[a] boiling point, °C [b] pour point, °C

TABLE 2
Symmetrical Aminoethyl Ether ECF

$R_2NCH_2CH_2OCH_2CH_2NR_2$		Yield	BP	PP
7. Me_2N-	C_8	<5%	-	-
8. Et_2N-	C_{12}	23%	178-80°	-80°
9. 	C_{12}	44%	175-85°	(-5° solid)
10. 	C_{12}	40%	170-85°	-85°
11. 	C_{14}	45%	207-19°	(-10° solid)
12. Pr_2N-	C_{16}	52%	225-40°	-60°
13. iPr_2N-	C_{16}	5%	-	-
14. Bu_2N-	C_{20}	20%	160°/20 torr	-40°

TABLE 3

Asymmetrical Aminoether ECF

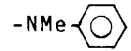
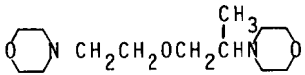
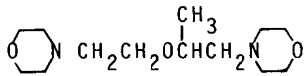
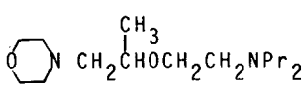
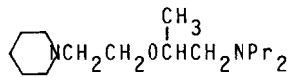
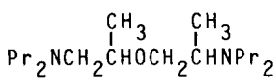
$R_2N-CH_2CH_2OCH_2CH_2-NR_2$			Yield	BP	PP
15. Me_2N-		C_{11}	6%	143-67°	-90°
16. Et_2N-		C_{12}	39%	175-85°	-80°
17. Et_2N-	$-NPr_2$	C_{14}	33%	195-200°	-75°
18. 	$-NPr_2$	C_{14}	42%	195-215°	-65°
19. Et_2N-		C_{15}	4%	195-230°	-70°
20. Et_2N-	$-NBu_2$	C_{16}	32%	215-30°	-50°

TABLE 4

Amino-isopropyl Ether ECF

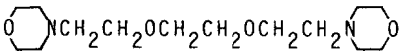
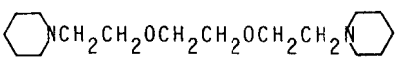
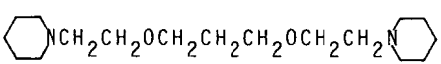
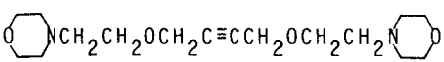
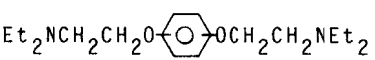
			Yield	BP	PP
21.	 [a]	C_{13}	35%	198-200°	-70°
22.		C_{13}	-	-	-
23.		C_{15}	38%	-	-
24.		C_{16}	19%	215-25°	-60°
25.	 [b]	C_{18}	33%	250-275°	-40°
26.	$Pr_2NCH_2CH_2CH_2OCH_2CH_2CH_2NPr_2$	C_{18}	18%	240-65°	-45°

[a] 21F contains 25% of the α-CF_3 isomer, 22F.

[b] 25F is derived from a mixture predominantly the α, β-dimethyl isomer.

TABLE 5

Diamino Diether ECF

		Yield	BP	PP
27. 	C_{14}	15%	200-15°	(-10° solid)
28. 	C_{16}	17%	220-40°	-65°
29. $Pr_2NCH_2CH_2OCH_2CH_2OCH_2CH_2NPr_2$	C_{18}	10%	255-85°	-65°
30. 	C_{17}	4%	210-60°	-
31. $Et_2NCH_2CH_2OCH_2C{\equiv}CCH_2OCH_2CH_2NEt_2$ [a]	C_{16}	15%	200-40°	-70°
32.  [a]	C_{16}	5%	224-30°	-
				
33. Ortho	C_{18}	20%	200-20°	-
34. Meta	C_{18}	22%	200-50°	-45°
35. Para	C_{18}	22%	220-250°	-
36. $Et_2NCH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2NEt_2$	C_{16}	8%	-	-
37. $Et_2NCH_2CH_2OCH_2CH_2\underset{\underset{Me}{|}}{N}CH_2CH_2OCH_2CH_2NEt_2$	C_{17}	4%	-	-

[a] The products of ECF 31F and 32F are fully saturated.

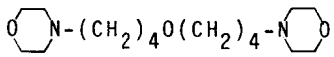
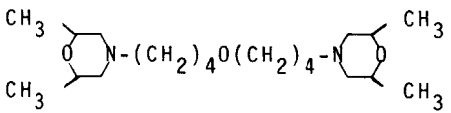
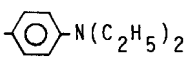
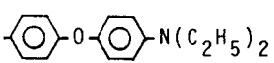
TABLE 6

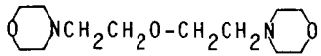
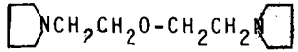
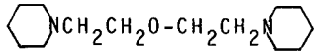
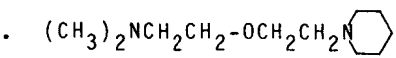
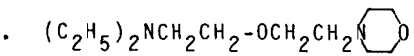
Monoaminoethyl ECF

		Yield	BP	PP
38. $CH_3CH_2CH_2OCH_2CH_2NPr_2$	C_{11}	15%	-	-
39. $nC_6H_{13}O\text{-}CH_2CH_2NEt_2$	C_{12}	10%	-	-
40. $nC_4H_9OCH_2CH_2OCH_2CH_2NEt_2$	C_{12}	3%	190-205°	-75°

TABLE 7

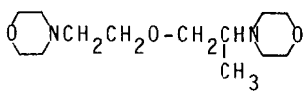
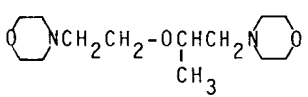
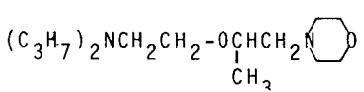
Aminoether Precursors [a]

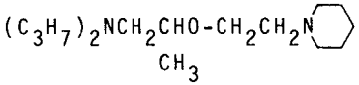
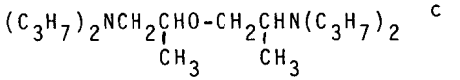
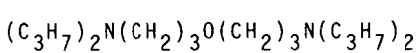
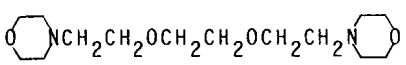
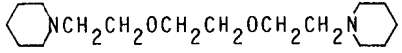
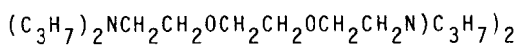
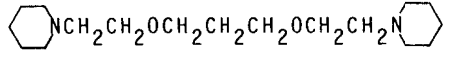
		BP/ Torr	Yield	Method
1.		150°/0.6	50%	B
2.	$(C_2H_5)_2$-N$(CH_2)_4$O$(CH_2)_4$-N$(C_2H_5)_2$	107°/0.3	70%	B
3.	$(C_3H_7)_2$-N$(CH_2)_4$O$(CH_2)_4$-N$(C_3H_7)_2$	165°/0.6	65%	B
4.		177.5°/0.7	25%	B
5.	$(C_2H_5)_2NCH_2CH_2$-O-  -N$(C_2H_5)_2$	140°/0.3	75%	A
6.	$(C_2H_5)_2$N-  -N$(C_2H_5)_2$	210°/.2	63%	B
7.	$(CH_3)_2NCH_2CH_2O$-$CH_2CH_2N(CH_3)_2$	98°/32	35%	A
8.	$(C_2H_5)_2NCH_2CH_2O$-$CH_2CH_2N(C_2H_5)_2$	77.5°/.6	70%	A

9.		120°/.7	84%	A
10.		94°/.8	40%	A
11.		135°/1.5	79%	A
12.	$(C_3H_7)_2NCH_2CH_2O\text{-}CH_2CH_2N(C_3H_7)_2$	125°/.6	47%	A
13.	$(iC_3H_7)_2NCH_2CH_2O\text{-}CH_2CH_2N(iC_3H_7)_2$	150°/0.8	74%	A
14.	$(C_4H_9)_2NCH_2CH_2O\text{-}CH_2CH_2N(C_4H_9)_2$	152°/.1	61%	A
15.		79°/.5	44-9%	A
16.		95°/.7	66%	A

(Continued)

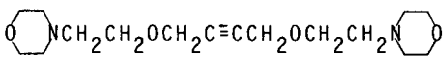
TABLE 7 (Cont.)

		BP/ Torr	Yield	Method
17.	$(C_3H_7)_2NCH_2CH_2O\text{-}CH_2CH_2N(C_2H_5)_2$	125°/.15	61%	A
18.	$(C_3H_7)_2NCH_2CH_2\text{-}OCH_2CH_2N$	125°/1.5	37%	A
19.	$(C_2H_5)_2NCH_2CH_2\text{-}OCH_2CH_2N(CH_3)$	141°/.4	83%	A
20.	$(C_2H_5)_2NCH_2CH_2\text{-}OCH_2CH_2N(C_4H_9)_2$	115°/.4	73%	A
21.	 [b]	128°/.15	40%	A
22.		116°/.05	27%	A
23.		120°/.6	55%	A

24.		102.5°/.18	40%	A
25.	 [c]	112°/.4	40%	A
26.			65%	B
27.		180°/.25		B
28.		142°/.6	59%	B
29.		145°/.2	79%	B
30.		131°/1.3	35%	A

(Continued)

TABLE 7 (Cont.)

	BP/ Torr	Yield	Method
31. a) $(C_2H_5)_2NCH_2CH_2OCH_2C{=}CCH_2OCH_2CH_2N(C_2H_5)_2$	140°/.6	68%	A
b) $(C_2H_5)_2NCH_2CH_2OCH_2CH_2CH_2CH_2OCH_2CH_2N(C_2H_5)_2$			
32. 	135°/.5		A
33. $(C_2H_5)_2NCH_2CH_2$-O-  -O-$CH_2CH_2N(C_2H5)_2$	150°/.6	73%	A
34. $(C_2H_5)_2NCH_2CH_2$-O-  -O-$CH_2CH_2N(C_2H_5)_2$	140°/.5	55%	A
35. $(C_2H_5)_2NCH_2CH_2$-O-  -O-$CH_2CH_2N(C_2H_5)_2$	170°/.7	75%	A
36. $[(C_2H_5)_2NCH_2CH_2$-$OCH_2CH_2]_2O$	104°/.3	30%	B
37. $[(C_2H_5)_2NCH_2CH_2$-$OCH_2CH_2]_2NCH_3$	155°/.3	49%	A

38.	$CH_3CH_2CH_2$-$OCH_2CH_2N(C_3H_7)_2$	45°/.8	41%	A
39.	$CH_3(CH_2)_5O$-$CH_2CH_2N(C_2H_5)_2$	55°/.3	55%	A
40.	$CH_3(CH_2)_3OCH_2CH_2O$-$CH_2CH_2N(C_2H_5)_2$	74°/.25	77%	A

Footnote: [a] The bond(s) being made are indicated by a dash (-).
[b] Compound 21 consists of 71% β-Me (shown) and 29% α-Me (compound 22).
[c] Compound 25 consists of 77%, α, β-Me_2 (shown); 13% β, β-, and 10% α, α.

beta isomer and traces of the alpha, alpha isomer. In Table 7,the bond being made is indicated by a dash (-), as illustrated below.

$$R_2NCH_2CH_2Cl + HOCH_2CH_2NR'_2 \longrightarrow \begin{cases} R_2NCH_2CH_2\text{-}OCH_2CH_2NR'_2 \\ + \\ (R_2NCH_2CH_2)_2O \end{cases}$$

$$R_2NCH_2CH(CH_3)Cl + HOCH_2CH_2NR'_2 \longrightarrow \begin{cases} R_2NCH(CH_3)CH_2\text{-}OCH_2CH_2NR'_2 \text{ (beta, major)} \\ + \\ R_2NCH_2CH(CH_3)\text{-}OCH_2CH_2NR'_2 \text{ (alpha, minor)} \end{cases}$$

$$R_2NCH_2CH(CH_3)Cl + HOCH(CH_3)CH_2NR'_2 \longrightarrow \begin{cases} R_2NCH(CH_3)CH_2\text{-}OCH(CH_3)CH_2NR'_2 \\ R_2NCH_2CH(CH_3)\text{-}OCH(CH_3)CH_2NR'_2 \\ R_2NCH(CH_3)CH_2\text{-}OCH_2CH(CH_3)NR'_2 \end{cases}$$

B. Alkylation of amines

This was useful for aminobutyl but not aminoethyl ethers, because reaction of 2-chloroethyl ether with amines gave instead the cyclic quaternary salt. The homologous triglycolyl dichloride did give the desired bis(dialkylamino)diethers.

$$R_2NH + Cl(CH_2)_4O(CH_2)_4Cl \longrightarrow R_2N\text{-}(CH_2)_4O(CH_2)_4\text{-}NR_2$$

$$R_2NH + ClCH_2CH_2(OCH_2CH_2)_nCl \longrightarrow R_2N^{\oplus}\!\!\bigcirc\!\!O \qquad n=1$$

$$R_2N\text{-}CH_2CH_2(OCH_2CH_2)_2\text{-}NR_2 \qquad n=2$$

Fluorination

Fluorinations were done in 5 through 100 amp cells at 5-7 volts much as described in Simons' patents [6]. The yields reported in Tables 1-6 are based on current and calculated on the amount of material boiling at the given range, or, in a few cases, on gc estimates of crude undistilled product. In many cases, the expected perfluorinated structure comprised as high as 70-90% of the material in the main distillation cut, accompanied by isomers and close homologs. We did not correct the reported yields, since our interest in these as inert fluids depends not on purity but only on boiling range. The fluorinated mixtures

are designated by an 'F' after the Arabic numeral of the hydrocarbon precursor.

This discussion will cover conductivity, product structure, structure-yield relationships, upper carbon content limit, hydride content, and pour points. Where available, literature results on ethers and amines will be compared to our aminoether results.

Conductivity

Lower dialkyl ethers give good conductivity, but at C_{10} and higher, tar formation leads to poor conductivity and eventually reaction termination [2]. Amines of up to C_{18} have been fluorinated with no mention of conductivity problems [2]. Most of the diaminoethers of Tables 1-5 ran with excellent conductivity, maintaining low voltage and forming only minor amounts of tars or high-boiling products. The presence of aromatic and acetylenic groups was associated with deteriorating conductivity and tar formation. The monoaminoethers ran very poorly, with rapidly decreasing conductivity.

Product Structure

Lower acyclic ethers are reported to undergo extensive cleavage to perfluoroacid fluorides and perfluoroalkanes, in addition to forming the perfluorinated ethers. Amines give generally the expected product accompanied by isomers and some higher and lower carbon content analogs. The aminoethers of this study electrofluorinate more like amines than ethers. Analysis of the gaseous products by gc-ir confirmed the formation of cleavage products such as CF_4, NF_3, C_2F_6, C_3F_8, and $C_2F_5OC_2F_5$ in most runs. Production of these materials was qualitatively higher in poor runs. Only minor cleavage to acid fluorides was seen in the gas or liquid products. The main fractions of the aminoethyl and aminoisopropyl ethers contained 70-90% of the expected structures, remarkably high structural purity for ECF products. In contrast, some of the poor-yielding products (diethers and materials $>C_{18}$) were complex mixtures with no major distillation plateaus, suggesting these were in part the products of cleavage and recombination. The products of ECF of compound 12 are shown below to illustrate points of cleavage.

ECF of $(C_3H_7)_2NCH_2CH_2OCH_2CH_2N(C_3H_7)_2$ (12)

Gas Products	Liquid Products	
C_3F_8 major	$(C_3F_7)_2N\text{-}CF_3$	4%
NF_3	$(C_3F_7)_2N\text{-}CF_2CF_3$	14%
COF_2	$(C_3F_7)_2N\text{-}CF_2COF$	trace
C_2F_6	$(C_3F_7)_2N\text{-}CF_2CF_2OCF_3$	6%
CF_3OCF_3	$(C_3F_7)_2N\text{-}CF_2CF_2OCF_2CF_3$	6%
$C_2F_5OC_2F_5$	$(C_3F_7)_2N\text{-}CF_2CF_2OCF_2CF_2N(CF_3)C_3F_7$	7%
	$(C_3F_7)_2N\text{-}CF_2CF_2OCF_2CF_2N(C_2F_5)C_3F_7$	trace
	$(C_3F_7)_2N\text{-}CF_2CF_2OCF_2CF_2N(C_3F_7)_2$	50.5%

The success with the isopropyl derivatives (Table 4) was surprising since branched ethers and amines frequently cleave during ECF [7]. (Note the very low yield from compound 13, the isopropyl isomer of 12.) Isomerization of isoalkyl to normal chains has been cited as a general feature of ECF [8]. For example, isopropylpyrrolidine gave a 36% yield of product, in which about 25% was the straight chain isomer [9]. However, there was no detectable isomerization to the linear form ($-CF_2CF_2CF_2-$) during ECF of 21 (a 71% beta Me - 29% alpha Me ether). In fact, this gave a 75-25 mixture of the corresponding perfluoroaminoethers, emphasizing the retention of structural integrity.

Structure-yield relationships

The Simons ECF process requires high voltages relative to those employed in organic electrochemistry. Under these high energy conditions, there are many paths available for each molecule and less regularity might be expected. One goal of this study was to establish whether useful structure-yield relationships exist for the organic reactants of ECF. In the several reviews extant on Simons ECF, few such data exist for acyclic ethers, probably because most yields are low. Lower alkyl groups on amines give roughly similar yields in various laboratories, but the series reported are small and there is some disagreement on the order of preference. Cyclic amines generally give better yields than acyclic. In our work, some trends were discernable. The amine groups associated with high yields were:

di-n-propylamino, piperidino, morpholino, pyrrolidino;
with moderate yields:

diethylamino, di-n-butylamino, 2,6-dimethylmorpholino;
with low yields:
dimethylamino, di-isopropylamino, N-methylanilino.

These trends are consistent with the scattered data on amines in the literature. The most surprising results were the low yields associated with methylamines 7, 15, and 19.

The linking groups associated with high yields are:
N-CH_2CH_2-O, N-$CH_2CH(CH_3)$-O, N-$CH(CH_3)CH_2$-O;
with moderate yields:
N-$CH_2CH_2CH_2$-O, O-$CH_2CH_2CH_2CH_2$-O, O-C_6H_4-O, N-C_6H_4-O;
and with low yields:
O-$CH_2C{=}CCH_2$-O, O-$CH_2CH_2CH_2CH_2$-O, non-aromatic diethers.

The success of the alpha- and beta-methyl aminoethers is in sharp contrast to the failure of the isopropylamine 13. Apparently being in a chain minimizes cleavage at branched points. The acetylenic diether proved initially superior to the saturated analog as a precursor to 31F.

Within the aminoethyl series, yields of some asymmetrical compounds could be estimated from those of their symmetrical parents. For example, 9 (44%) and 12 (52%) predict 48% for 18 (42%); 8 (23%) and 9 (44%) predict 34% for 16 (39%); 8 and 12 predict 38% for 17 (33%). More significant to use of these observations, introduction of a second heteroatom to the alkylene led to reduced, less predictable yields. As Table 5 indicates, attempts to combine the favorable features into diethers were only moderately successful. The aromatic compounds (33-35) and the triglycolyl dichloride products (27-29) all gave about 20% yields. The addition of a central -CH_2- to 28, giving 30, lowered the yield to 4%. A similar decrease was seen in the monoether series, comparing 12 and 26. These data show that the length of the carbon units is equally as crucial to good yields as the number of heteroatoms.

The monoaminoether series (Table 6) indicates that the stabilizing influence of the amino group does not extend past the O and in fact the result is worse than expected for a simple ether.

Carbon content

The yields observed were very good through C_{20} (compound 14) in the aminoethyl ethers, especially when compared to literature reports of 3% for C_{18} amines. Generally, the yields of the expected products were decreasing by C_{18}. In some examples, the complex mixtures probably contain materials with less than the expected number of C atoms. This decrease in yield with increased C-content is in keeping with results in other series, but the upper limit of useful yields is higher for these aminoethers.

Hydrogen retention

Very little data have been reported on this subject. We will not report on this in detail here, but did observe hydrogen contents of < 0.01 to 1.5 mg/g., generally higher with increased molecular weight and with poor runs. For some applications, the fluids reported here would require treatment with caustic to remove these impurities.

Pour points

The estimated pour points (pp) of most of the diaminomonoethers were 30-40°C lower than those of commercial (3M) inert fluids of similar C content:

FC-43 (bp 174°C) literature pp -50°C [10], -50°C by our technique vs 2F (bp 178°C) pp -80°C and 5F (bp 175-85°C) pp -80°C

FC-70 (bp 215°C) literature pp -25°C [10], -30°C by this technique vs. 24F (bp 215-25°C) pp -60°C and 20F (bp 215-30°C) pp -50°C

FC-71 (bp 253°C) pp 33°C [10]; vs. 26F (bp 240-65°C) pp -45°C and 25F (ca. 250°C) pp -40°C.

In contrast, the symmetrical bis(cycloaminoalkyl) ethers (compounds 1F, 9F, and 11F, but not 10F) solidified at -10 to

0°C. Diether 27F (but not 28F) also solidified. A 50-50 w/w mixture of 9F and 11F gave a pour point of -65°C, indicating that if the crystal lattice could be disturbed, the typical pour point (solidifying to a glassy state) could be reached. A 50-50 mixture of 8F and 9F gave a pour point of -70°C, and of 27F and 28F gave -50°C. This result led to synthesis of asymmetrical ethers such as 16F and 18F, which also had low pour points. Likewise, addition of a methyl group to 9F (compound 21F) gave a low pour point (-70°C). The alpha, beta dimethyl analog (25F) of the non-crystallizing fluid 12F (pp -60°C) had a pour point of -40°C, only slightly higher than that of the linear isomer 26F (pp -45°C). Diethers 28F and 31F have pour points only slightly lower than that of the C_{16} monoether 12F, while the cyclohexane-linked compounds 33F-35F are considerably higher.

CONCLUSION

We conclude that under excellent operating conditions that a level of predictability is possible but not certain in Simons ECF. Trends but not rules can be discerned in these data. The most attractive mechanism proposed for ECF is the four-step EC_bEC_N sequence (radical-cation, radical, cation and capture of the cation by fluoride) [12]. Support for this was recently found in the ECF of several compounds, including isobutyryl fluoride (isomerization) and N-methyl morpholine (fluorination apparently begins alpha to oxygen) [8]. Such intermediates offer a possible explanation for the difference in yields between the aminoethyl ethers and the amino-n-propyl ethers.

$R_2N\text{-}(CH_2)_n\text{-}CH_2^{\bullet\oplus}OR$ $R_2N\text{-}(CH_2)_n\text{-}\dot{C}HOR$ $R_2N\text{-}(CH_2)_n\text{-}CH^{\oplus}OR$ n=1 vs. 2

The cationic forms differ in the possible cleavage products - the amino-n-propyl group can cleave to a vinyl ether (which would then polymerize in the HF, possibly accounting for the tarring noted), while the aminoethyl group would yield a carbene fragment, a less favorable pathway.

$$R_2NCH_2CH_2CH^{\oplus}OR \longrightarrow R_2NCH_2^{\oplus} + CH_2{=}CHOR$$

$$R_2NCH_2CH^{\oplus}OR \longrightarrow R_2NCH_2^{\oplus} + CHOR$$

However, the lack of isomerization of the aminoisopropyl ethers to the n-propyl form could be initially taken as evidence against this mechanism. The fluorinations of 21 and 22 illustrate the complexity of mechanistic arguments possible. Neither material produced any n-propyl product, giving apparent retention of structure. Assuming that the positions alpha to the oxygen are fluorinated first, the cations involved in isomerization would be:

$$R_2N\underset{\oplus CH_2}{CH}CF_2OR \not\longrightarrow R_2NCH_2CH_2CF^{\oplus}OR$$

$$R_2N\underset{\oplus CH_2}{CH}CF_2OR \not\longrightarrow R_2NCH^{\oplus}CH_2CF_2OR$$

The lack of isomerization implies the migratory aptitudes of the R_2NCH_2- (in the alpha) and $ROCF_2$- (in the beta isomer) are low relative to capture of fluoride. An intriguing alternative is that isomerization does occur, via a 4-membered ring involving the heteroatom, yielding the other isomer in each case. Capture of a cation by oxygen yielding 5- and 6-membered rings is well known, but 4-membered rings and N-rings are not [2]. The nmr structural assignments argue against a single isomerization and the product purities against double, undetectable changes. Further work on ECF and other electrochemistry of these aminoisopropyl ethers may help test the mechanism of ECF.

The pragmatic outcome of this study is a series of new perfluorinated fluids having lower pour points than currently available fluids. For the aminoethyl ethers, both the hydrocarbon precursor synthesis and electrofluorination yields are very good. Relatively minor changes in structure led to large and unpredictable changes in ECF yields.

EXPERIMENTAL

Distillations were done using 3- or 6- plate Snyder columns. Gc analyses of fluorocarbon gases were performed on Carbopack columns; those of liquid hydrocarbon and fluorocarbon products on SE-52, all on HP 5780 and 5980 instruments. Gc-ms data were obtained primarily with methane positive chemical ionization, with supporting data in some cases from argon NCI and electron impact (EI), on an HP-5985B. Nmr spectra were obtained using an IBM Model NR-100/AF. The F-nmr data were acquired at 94 MHz, using $CFCl_3$ as solvent. The F-nmr chemical shifts are expressed in terms of (-) ppm upfield of internal $CFCl_3$.

Proton nmr data were acquired at 100.13 MHz, using $CDCl_3$ as solvent. All H-nmr chemical shifts are expressed in terms of (+) ppm δ downfield of internal TMS.

Carbon-13 nmr data were acquired at 25.2 MHz, using $CDCl_3$ as solvent. All C-13 nmr chemical shifts are expressed in terms of (+) ppm δ downfield of internal TMS.

Pour points

These were estimated by chilling ca. 4 ml of the fluid in a small vial below the glass point and allowing to slowly warm up while observing the fluid melt from the bulb of a thermometer initially immersed in the liquid. Several symmetrical molecules crystallized after passing through this pour point region, indicating the material was supercooled initially. In these cases, the melting points were fairly broad (-10 to +10°C typically).

Precursor synthesis. Method A.

(PTC Williamson ether synthesis) This route is exemplified with bis[2-(dipropylamino)ethyl] ether (12). Treatment of di-n-propylamine in methanol with gaseous ethylene oxide gave a mildly exothermic conversion to the corresponding aminoethanol. Part of this was converted, by heating with thionyl chloride 6 hours and then washing with cold base, into the aminoethyl

chloride. A mixture of 2-di-n-propylaminoethanol (743 g, 4.5 mol), 1800 g of 50% NaOH (22.5 mol), 10 g Adogen 464 quaternary ammonium salt, and 2 liters of THF was treated with 653 g (4.5 mol) of di-n-propylaminoethyl chloride, and the resulting mixture was heated at reflux for 6 hours. After cooling, the organic layer was separated, washed with water, and dried in methylene chloride over $MgSO_4$. Distillation on a 3-plate Snyder column afforded 920 g (3.38 mol, 75%) of the product, bp 120-5°C at 0.5 torr. The H-nmr spectrum was consistent with the desired structure (12):

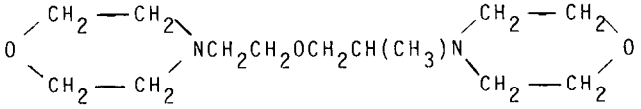
$[(CH_3CH_2CH_2)_2N\text{-}CH_2CH_2\text{-}]\text{-}O$
a b c d e

a 0.9 (t); b 1.45 (sextet); c 2.4 (t); d 2.6 (t); e 3.5 (t)
The C-13 nmr spectrum was assigned as follows:
a 11.9; b 20.6; c 57.2; d 53.8; e 69.9

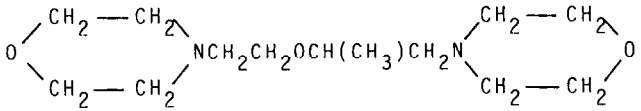
Beta-methyl bis[2(4-morpholino)ethyl] ether (21)

A solution of 261 g (3.0 mol) morpholine in 600 ml methanol was treated with 174 g (3.0 mol) propylene oxide, resulting in an exotherm to 45°C. At 3 hours, the conversion was complete. The methanol was stripped off and the product was distilled to 393 g (90%), bp 65-70°C/4 torr. H-nmr data showed a mixture of 96% alpha - and 4% beta-methyl morpholinoethanols. The structures were unambiguously assigned and quantified by measurement of the alpha and beta-methyl doublet resonances at 1.13 and 0.95 ppm (downfield of TMS) respectively. Addition of 170 ml (2.15 mol) $SOCl_2$ dropwise to 300 g (2.0 mol) of the above alcohol resulted in a solid mass. This was diluted with 100 ml $SOCl_2$ and heated at reflux for 2 hours. The mixture was stripped and the residue heated with 500 ml ethanol for 2 hours. Trituration with ether and treatment of the solid formed with dilute aqueous base yielded a tan liquid, extracted with ether and stripped. This was treated with 262 g (2.0 mol) 2(4-morpholino)ethanol in the above phase-transfer catalysed Williamson reaction. Workup gave 201.6 g (40%) of liquid bp 126-9°C/0.15 torr. GLC indicated a 29-71% mixture of two similar materials, the smaller eluting first.

The proton and C-13 nmr (in $CDCl_3$) were consistent with the assignments of 71% beta-29% alpha methyl, as follows:



beta



alpha

The H-nmr assignments (ppm δ) are: 2.2-2.7 (b,c,g,h,k,l,p,q as overlapping multiplets); 3.3-3.8 (a,d,e,i,j,m,o,r as multiplets); 1.10 (f, as 6.0 Hz doublet); 1.20 (h, as 6 Hz doublet). The latter two resonances in a ratio of 71 (1.10 ppm) to 29 (1.20 ppm) allowed assignment of these isomers as the beta- and alpha- methyl isomers, respectively. The C-13 nmr spectrum was assigned: 66.9(a,j,r); 54.1(b,k); 58.2(c); 68.9(d); 73.2(e); 13.1(f); 58.9(g); 49.8(h); 66.4(i); 58.6(l); 66.3(m); 18.4(n); 73.5(o); 64.5(p); 54.4(q). The methyl carbon lines of 13.1 ppm (beta) and 18.4 ppm (alpha) allowed unambiguous assignment of structures 21 and 22. EIms confirmed these assignments. The alpha isomer (22) yields a fragment of M/e=100 as the base peak (R_2N-CH_2+) from both sides of the ether, while the beta isomer (21) yields the 100M/e fragment plus one at 114M/e as the base peak, corresponding to R_2N-$CH(CH_3)$+.

Alpha-methyl-bis[2(4-morpholino)ethyl] ether (22)

A mixture of 786 g (6.0 mol) 2(4-morpholino)ethanol and 510 ml (6.45 mol) $SOCl_2$ was heated at reflux for 2 hours and worked up as in the above example to give 563 g (3.75 mol) morpholinoethyl chloride. This was condensed with 543 g (3.75 mol) alpha-methyl 2(4-morpholino)ethanol in the PTC Williamson synthesis to give a mixture containing by GLC 38% unreacted alcohol, 13% bis(morpholino)ethyl ether, and 45% the desired

ether. Distillation afforded 250.0 (27%) of a liquid bp 116°C/0.05 torr containing 95% of the desired alpha-methyl ether, 3% of morpholinoethyl ether, and 2% of the beta-methyl ether.

Alpha, beta-dimethyl-bis[2(di-n-propylamino)ethyl] ether (25)

In a similar fashion as above, dipropylamine was reacted with propylene oxide to give a 98.5-1.5% mixture of the alpha and beta methyl dipropylaminoethanols, confirmed as isomers by gc/ms at 159. Part of this was treated with $SOCl_2$ and the resulting chloride was reacted with the remaining alcohol in the PTC reaction. Workup gave a 38% yield of a liquid bp 108°C/0.15 torr. This was proven by gc/ms to consist of three isomers, identified as α,β-(77%); β,β-(13%); and α,α-(10%).

α, β -$(CH_3CH_2CH_2)_2$-NCH$(CH_3)$$CH_2OCH(CH_3)$$CH_2N(CH_2CH_2CH_3)_2$
a b c d e f g h i j k l

The H-nmr spectrum was assigned as follows:
a, l 0.9 (t); b, k 1.45 (sextet); c, j 2.4 (t); d 2.9 (m); e 1.0 (d); f, g 3.05-3.7 (m); h 1.15 (d); i 2.1-2.65 (AB quartet).

The C-13 nmr spectrum was assigned as follows:
a, l 11.6; b 22.5; c 53.0; d 55.3; e 13.1; f 72.2; g 75.0; h 18.8; i 60.7; j 57.4; k 20.7.

β, β -[$(CH_3CH_2CH_2)_2$-NCH$(CH_3)$$CH_2$]$_2$-O
a b c d e f

The H-nmr spectrum was assigned as follows:
a 0.9 (t); b 1.45 (sextet); c 2.4 (t); d 2.9 (m); e 1.0 (d); f 3.4 (m).

The C-13 nmr spectrum was assigned as follows:
a 11.9; b 22.6; c 53.0; d 55.0; e 13.1; f 74.6.

α, α-[$(CH_3CH_2CH_2)_2$-NCH_2CH(CH_3)]$_2$-O
a b c d e f

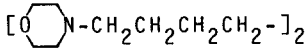
The H-nmr spectrum was assigned as follows:
a 0.9 (t); b 1.45 (sextet); c 2.4 (t); d 2.1-2.65 (AB quartet); e 3.35 (m); f 1.15 (d).

The C-13 nmr spectrum was assigned as follows:
a 11.6; b 20.8; c 57.5; d 61.4; e 72.7; f 20.0.

Identification of the β, β-isomer was facilitated by its synthesis. A mixture of 177.4 g (1.0 mol) of the alkyl chloride from $Pr_2NCH_2CH(CH_3)OH$ and $SOCl_2$, 400 g (5 mol) 50% NaOH, 300 ml dioxane, and 0.5 g Adogen 464 was stirred at reflux 16 hours and worked up as above to give 102.2 g (34%) of a liquid, bp 108°C/0.15 torr. This mixture proved by gc/ms a mixture of β,β - (61%); α, β-(36%); and α, α-(3%) isomers.

Precursors. Method B. Alkylation of amines.

This route is exemplified with bis(4-morpholinobutyl) ether, the precursor to 1. A mixture of 1200 ml (13.8 mol) morpholine and 1.2 liters of denatured ethanol was treated with 628 g bis(4-chlorobutyl) ether [13] (3.0 mol) with no obvious change. The mixture was heated at reflux for two days, quenched in 1 liter H_2O, and the organic layer separated. The H_2O was washed with methylene chloride and the combined organic layers dried over $MgSO_4$ and distilled on a short path to 616.7 g (68.5%) of product, bp 160-70°C at 0.3-0.6 torr. The H-nmr is consistent with the desired structure:



a 3.65 (t); b 2.4 (t); c 2.3 (t); d and e 1.55 (m); f 3.4 (t).

Fluorination

The aminoethers were generally dissolved in anhydrous HF at ca.30% by wt. and these solutions were charged periodically to Simons cells of 1, 10, 30, and 40 amp capacities. The concentration of organic material in the cell was maintained between 5-15%. Cell voltage was generally 5-6.6 volts through the run. The temperature was usually 20-50°C. Most of the product was drained periodically from the bottom of the cell pot.

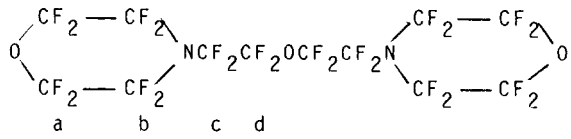
Some lower boiling liquids were recovered from the condenser. Gaseous products were analyzed by GC-IR. The liquid products were combined, treated with NaF, and fractionated. Tables 2-6 contain the starting structure, the boiling and pour points, and the distilled yields. These yields are in close agreement with the current yields calculated on a daily basis by GLC of the cell drainings, and hence represent an average of many experiments in the same equipment. Those runs which were repeated in different equipment gave good agreement in yield and composition. Gc-ms and F-nmr were used to characterize most of these main fractions. ECF of 9 and of 12 is described in detail below, followed by analytical data on most of the products.

ECF of bis[2(4-morpholino)ethyl) ether (9)

A 20 amp electrochemical cell was charged with 750 g anhydrous HF. A total of 891 g (3.43 mol) of bis(2-morpholino-ethyl) ether (9) was added periodically over 233 hours to the cell. HF was added as needed to replace that consumed in the reaction and also lost through the condensing system. The cell was operated continuously at an average of about 5.8 volts, 20 amps, 50°C, and 30 psig. The perfluorinated liquid product mixture, present as a lower layer in the cell and in the overhead condensing system, was periodically drained off to give a total of 1581 g. Of these drainings, 1467.4 g were treated with NaF to remove HF and then fractionated on a 3-plate Snyder column to 1015 g (44% yield on current, 44% yield on organic) bp 175-85°C. This on supercooling in liquid N_2 to a glassy solid and allowing to warm, becomes a thin liquid at ca. -80°C and then solidified to a white solid, mp. -5°C. H-nmr showed less than 0.05 mg/g of residual hydrogen atoms.

Gc-ms showed that 81% of the main fraction was the desired product, with 657 M/e (parent-F); 330 (Morph-CF_2CF_2+); 308 (Morph-CF_2CO+); 280 (Morph-CF_2+).

The F-nmr spectrum was assigned as follows:



a(-87.7); b(-92.7); c(-95.8); d(-88.1).

ECF of bis[2(dipropylamino)ethyl] ether (12).

A 100 ampere electrochemical cell was charged with 2300 g anhydrous liquid HF. A solution of 2100 g of bis[2-(dipropylamino)ethyl] ether in 955 g HF was periodically added over 269 hours to the cell, along with additional HF as needed to replace that consumed in the reaction and also lost through the condensing system. The cell was operated continuously at an average of about 6 volts, 60 amps, 55°C, and 30 psig. The perfluorinated liquid product mixture was periodically drained off to give a total of 5120 g of cell drainings. These were treated with NaF to remove residual HF, filtered, and distilled on a 3-plate Snyder column to yield a total of 3900 g (52% yield on current, 55% on organic) of a main cut boiling in the range o 225-240°C. A small sample was heated with KOH (3 parts) and H_2O (1 part) for 20 hours.

Gc-ms showed that 78% of the main fraction was the desired product, with 901 M/e (parent-F); 568 (parent-N-$(CF_2CF_2CF_3)_2$); 452($(C_3F_7)_2NCF_2CF_2^+$). 169 M/e ($CF_3CF_2CF_2^+$) was the longest straight chain fragment observed.

The F-nmr spectrum was assigned as follows:

$(CF_3CF_2CF_2)_2$-$NCF_2CF_2OCF_2CF_2N(CF_2CF_2CF_3)_2$
a b c c e

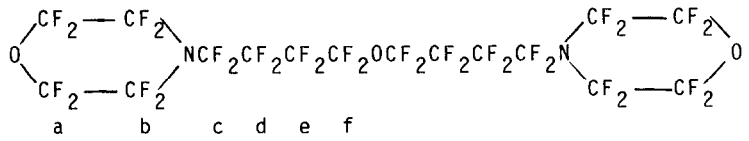
a(-81.8); b(-121.6); c(-84.8); d(-88.0); e(-82.2).

The major impurities were the parent minus one and two CF_2 groups.

The following fluorinated products were analyzed by F-nmr and gc/ms. All other reaction products were characterized only by F-nmr (data not shown).

Perfluoro-bis[4(morpholino)butyl] ether (1F)

Gc-ms showed 69% of the main fraction to be the desired product, with diagnostic fragments as follows: 857M/e(parent-F); 430 (morph-$(CH_2)_4$+); 408 (morph-$(CH_2)_3$CO+); 280 (morph-CH_2+). The F-nmr was assigned as follows:



a(-87.7); b(-92.4); c(-90.5); d(-123.5); e(-125.9); f(-83.3).

Perfluoro-bis[2(diethylamino)ethyl] ether (8F)

Gc-ms showed that 91% of the main fraction was the desired product, with 701 M/e(p-F); 468($(C_2F_5)_2NCF_2CF_2OCF_2CF_2$+); 352($(C_2F_5)_2CF_2CF_2$+); and 302($(C_2F_5)_2NCF_2$+).

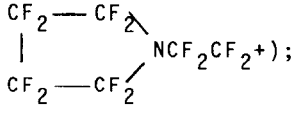
The F-nmr spectrum was assigned as follows:

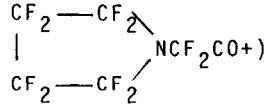
$(CF_3CF_2)_2$-$NCF_2CF_2OCF_2CF_2N(CF_2CF_3)_2$
a b c d

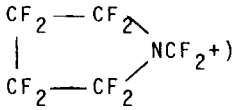
a(-81.4); b(-89.2); c(-89.2); d(-82.9).

Perfluoro-bis[2(1-pyrrolidino)ethyl] ether (10F)

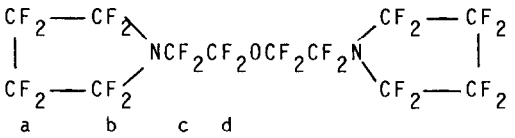
Gc-ms showed that 88% of the main fraction was the desired product, with 625 M/e (parent-F);

314 

292 

264 

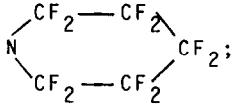
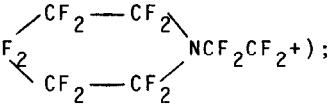
The F-nmr spectrum was assigned as follows:

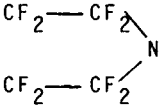


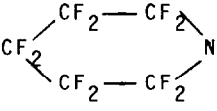
a(-133.3); b(91.0); c(-97.0); d(-86.8)

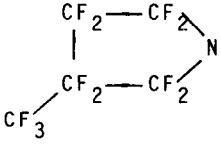
Perfluoro-bis[2(1-piperidino)ethyl] ether (11F)

Gc-ms confirmed that the product was consistent with the structure of the desired product, with 725 M/e (parent-F);

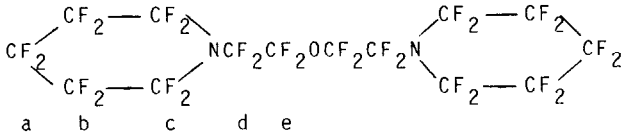
480 (parent -  ; 364 ( ;

342 ( .

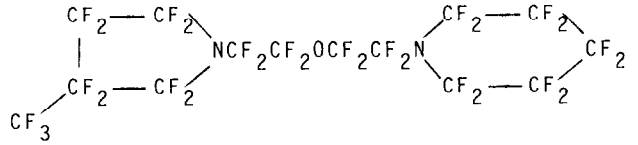
However, gc/ms could not distinguish between  and

 end groups.

The F-nmr data indicated ca. 70% of the main fraction was desired product and ca. 30% was a ring-contracted isomer. The F-nmr specrum was assigned as follows:



a b c d e



f g h d e

a(-134.6); b(-132.3); c(-91.3); d(-94.8); e(-88.0); f(-73.2); g(-183.7); i(-120 to -143 as AB quartet); h, j(-80 to -103 as A quartets).

Perfluoro-bis[2(di-n-butylamino)ethyl] ether (14F)

Gc/ms indicated that 75% of the sample was desired product. In this case, 1101 M/e (parent-F) was not detected due to the mass limitation of the instrument (1000), however,

863($(C_4F_9)_2NCF_2CF_2OCF_2CF_2NCF_2CF_2CF_2CF_2^+$);

668($(C_4F_9)_2NCF_2CF_2OCF_2CF_2^+$); 552($(C_4F_9)_2NCF_2CF_2^+$) and

219($C_4F_9^+$) indicated the presence of the target compound.

The F-nmr spectrum was assigned as follows:

$(CF_3CF_2CF_2CF_2)_2$-$NCF_2CF_2OCF_2CF_2N(CF_2CF_2CF_2CF_3)_2$

a b c d e f

a(-81.5); b(-127.1); c(-118.7); d(-84.5); e(-88.0); f(-82.3).

Perfluoro-2(diethylamino)ethyl 2(di-n-propylamino)ethyl ether (17F)

F-nmr data indicated the major component in the main fraction was the desired product. The F-nmr spectrum was assigned as follows:

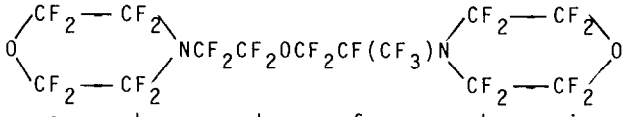
$(CF_3CF_2CF_2)_2$-$NCF_2CF_2OCF_2CF_2N(CF_2CF_3)_2$
a b c d e f g h i

a(-81.6); b(-121.3); c(-84.4); d(-87.8); e, f(-82.1); g(-88.7); h(-88.7); i(-81.1).

Perfluoro-beta-methyl-bis[2(morpholinoethyl)] ether (21F)

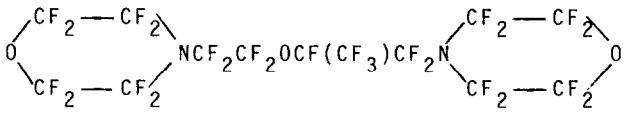
Gc/ms indicated that the main fraction was the desired product with 707 M/e (parent-F); 496 (parent-morph); 380 (morph-C_3F_6+); 330 (morph-C_2F_4+); 358 (morph-C_3F_4O+); 308 (morph-C_2F_2O+). However, it was not possible by gc/ms to distinguish between -O-CF_2-$\underset{CF_3}{CF}$-morph and -O-$\underset{CF_3}{CF}$-CF_2-morph using this technique.

The F-nmr data indicated ca. 75% of the main fraction was the desired beta-oxygen branch product and ca. 25% was the isomeric alpha-oxygen branch product. The F-nmr was assigned as follows:



a b c d e f g h i

beta



j k l m n o p q r

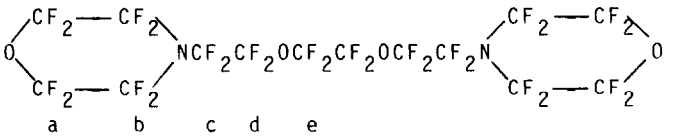
alpha

a,j,r(-87.6); b,k,q(-92.7); c,l(-95.6); d,m,o(-79.5 to -85); e,p(-81 to -93 as AB quartets); f(-158.3); g(-75.5); h,i(-81 to -93: axial-equatorial AB quartets); n(-144.9).

Perfluoro-1,2-bis(2-morpholinoethoxy)ethane (27F)

Gc-ms showed that 77% of the sample was the desired product, with 773 M/e (parent-F); 446 (morph-$CF_2CF_2OCF_2CF_2$+) 424 (morph-$CF_2CF_2OC_2F_2O$); 330 (morph-CF_2CF_2+); 308 (morph-C_2F_2O+); and 280 (morph-CF_2+).

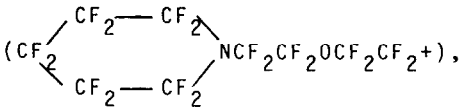
The F-nmr spectrum was assigned as follows:



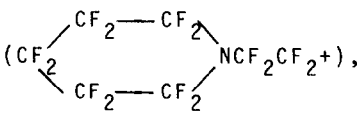
a(-87.7); b(-92.7); c(-96.0); d,e(-88 to -89.3).

Perfluoro-1,2-bis(2-piperidinoethoxy)ethane (28F)

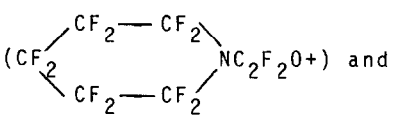
Gc/ms shows that 74% of the main fraction is the desired product with 841 M/e (parent-F),

480 

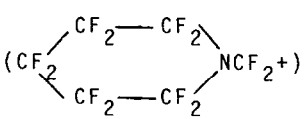
),

364 

),

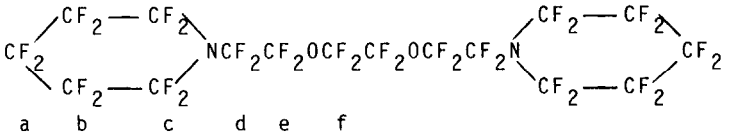
342 

and

314 

as supporting fragmentation.

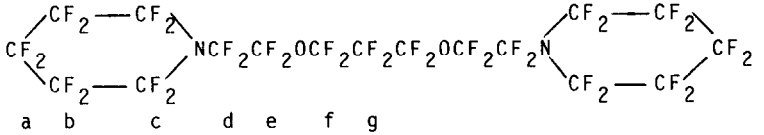
The F-nmr spectrum was assigned as follows:



a (-134.7); b (-132.3); c (-91.3); d (-95.0); e,f (-88.5 and -89.0).

Perfluoro-1,3-bis(2-piperidinoethoxy)propane (30)

F-nmr data indicated approximately equimolar relative amounts of desired product and 11F were present. The F-nmr spectrum was assigned as follows:



a(-134.7); b(-132.5); c(-91.6); d(-94.9): e(-88.3); f(-83.8); g(-129.3).

Perfluoro-1,4-bis(2-diethylaminoethoxy)butane (31F)

Gc/ms showed that the desired product is present, with 917 M/e (parent-F); 352($(CF_3CF_2)_2NCF_2CF_2^+$); 302($(CF_3CF_2)_2NCF_2^+$), 119($CF_3CF_2^+$).

The F-nmr spectrum was assigned as follows:

$(CF_3CF_2)_2$-$NCF_2CF_2OCF_2CF_2CF_2CF_2OCF_2CF_2N(CF_2CF_3)_2$

a b c d e f

a(-81.5); b(-89.3); c(ca.-89.3); d,e(-82.6 and -83.8); f(-125.9).

ACKNOWLEDGEMENTS

This paper is dedicated to the memory of Joseph H. Simons, the inventor of the ECF process. We also thank Charles M. Leir for many illuminating discussions of this work.

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