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O-Hydroxyethylation of 1,1-dihydroperfluorinated alcohols

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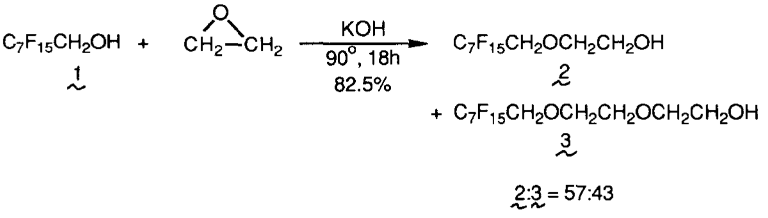
Abstract

A convenient transformation of 1,1-dihydroperfluorinated alcohols into *O*-hydroxyethyl derivatives ($R_FCH_2OCH_2CH_2OH$) is described in which ethylene carbonate is utilized as the alkylating agent. Tetraalkylammonium iodides and trialkylamines are effective catalysts.

Introduction

O-Hydroxyethylation of 1,1-dihydroperfluorinated alcohols has most often been conducted using ethylene oxide [1]. Aside from the obvious problems of handling a toxic*, explosive [3] and gaseous reactant, polyalkylation side-reactions can also be significant. In one procedure [1e], for example, despite employing only 20% stoichiometric excess of ethylene oxide, a 57:43 mixture of mono- (**2**) and bis- (**3**) derivatives of 1,1-dihydroperfluorooctanol (**1**) was obtained [eqn. (1)].



(1)

By-product **3** resulted from the relatively high reactivity of ethylene oxide and its inability to effectively discriminate between starting and product alcohols.

Often it is desirable to transform relatively acidic 1,1-dihydroperfluorinated alcohols (whose monomeric and polymeric acyl derivatives are hydrolytically labile) into less acidic *O*-hydroxyalkylated alcohols. Polyalkylation can be especially disadvantageous because the weight fraction of valuable fluorine in the product goes down correspondingly.

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*The TLV for ethylene oxide over an 8-h period is 1 ppm and the compound is a suspected human carcinogen [2].

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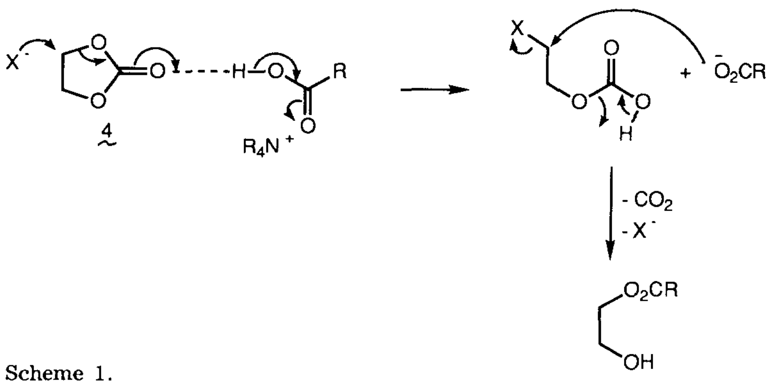

Scheme 1.

Ethylene carbonate (**4**), a relatively non-toxic, low-melting solid* [4], has been utilized effectively with hydroxyethylate phenols [5a,b,c], thiophenols [5a], thiols [5a], carboxylic acids [5a,c,d], certain heterocyclic compounds [5c], acid anhydrides [5c,e] and perfluoroalkane sulfonamides [5f]. Hydroxyethylation of simple alcohols [5a,g] and amines [5a] has also been reported but in rather low yield. These latter reactions may be complicated by competitive attack at the carbonyl group of **4** leading to carbonate [5g,h] and carbamate [5i,j] products, respectively.

A proposed reaction mechanism for hydroxyethylation using **4** [5e] is illustrated in Scheme 1 with a carboxylic acid substrate and a tetraalkylammonium halide catalyst. It involves initial acid–base interaction between the carbonyl oxygen in **4** and an acidic hydrogen of the substrate.

That useable substrates for hydroxyethylation have been relatively acidic compounds suggested the potential suitability of 1,1-dihydroperfluorinated alcohols for the reaction. Fluorinated alcohols are approximately 1000-times more acidic than the corresponding non-fluorinated alcohols [6]. We now report the successful *O*-hydroxyethylation of 1,1-dihydroperfluorinated alcohols using **4****.

Results and discussion

It was decided to use an excess of **4** and a tetraalkylammonium halide catalyst [5e] which was soluble in the **4**/fluorocarbon medium and could be removed from the product by extraction into water. Reaction temperatures of *c.* 140 °C had been required in other hydroxyethylations [5e], and so the first experiments were with fluorinated alcohols having boiling points >140 °C. Use of a sealed system at pressures in excess of atmospheric seemed inappropriate. Also, there is an upper limit to the reaction since **4**

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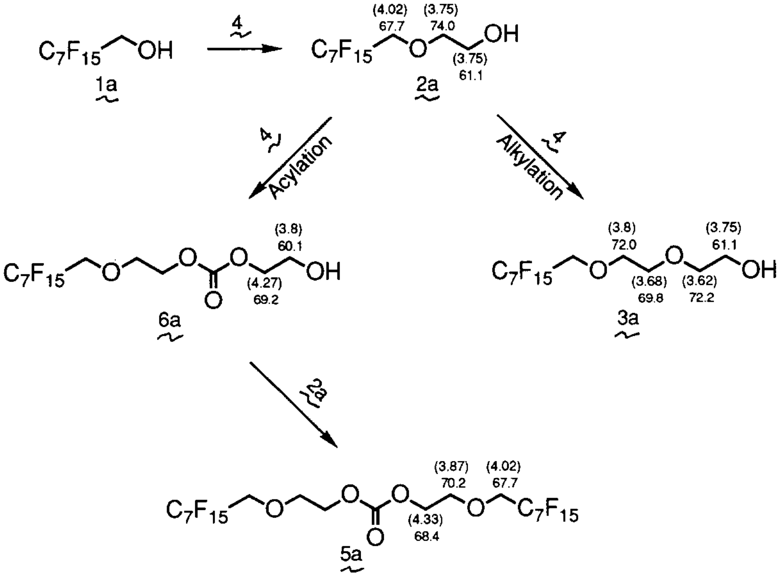
*Oral rat $LD_{50} = 10$ g kg^{-1} [4a]. Ethylene carbonate was shown not to be carcinogenic under test conditions in one study [4b].

**A preliminary report of this work has appeared [7].

is known [8] to product ethylene oxide above 180 °C in the presence of tetraalkylammonium halides.

The hydroxyethylation reaction was first successfully applied to 1,1-dihydroperfluorooctanol (**1a**; b.p., 146 °C) using a 0.5 equiv. excess of **4** and tetramethylammonium iodide (2 mol% based on **1a**) as the catalyst. The initial heterogeneous mixture of reactants liquefied to a brown solution at 90 °C, and, as expected, temperatures in the 120–140 °C range were required to evolve carbon dioxide at reasonable rates. As indicated by GC, *c* 95% conversion occurred after 48 h at 140 °C with some precipitation of the catalyst occurring in the later stages, apparently as a result of depletion of solubilizing **4**. The ^{1}H NMR spectrum showed several methylene resonances in the 3.5–4.5 ppm region, and four reaction products were identified from COSY and C—H heteronuclear correlations; three of these were isolated by fractional distillation. The major product (comprising 84% of the reaction mixture as established by NMR methods) was identified as the desired mono(*O*-hydroxyethylated) product **2a** and was isolated in 66% yield. Other isolated products were the bis(alkylated) product **3a** (7%) and the bis(acylated) product **5a** (6%). Product **5a** resulted from acylation of **2a** by **4**, initially generating **6a**. Compound **6a** was barely detected (3% by NMR spectroscopy); however, because of the well-known propensity for transesterification of 2-hydroxyethyl ester derivatives [9], the bis(acylated) product **5a** was formed in the presence of excess **2a**. This sequence and relevant ^{1}H (in parentheses) and ^{13}C NMR assignments are shown in Scheme 2.

Tetramethylammonium iodide was not a completely satisfactory catalyst, since its precipitation from the reaction may have contributed to longer



Scheme 2.

reaction times and possibly to further alkylation and acylation. Therefore, tetraethyl-, tetra-n-propyl- and tetra-n-butylammonium iodides were examined as potential catalysts for the reaction, and the results of a comparative study with tetramethylammonium iodide are listed in Table 1.

All tetraalkylammonium iodides were of comparable efficiency, with the possible exception of tetramethyl which was partially removed from the reaction by precipitation. Probably as a result of the decreased reaction time (48 h to 22 h), the level of by-products was also reduced with every catalyst. In an attempt to decrease the amount of by-products still further, tetra-n-butylammonium iodides was used at twice the catalyst level and with only a 0.25 equiv. excess of **4**. However, by-products were not significantly reduced and conversion was adversely affected (entry 5). When the reaction temperature was increased from 140 °C to 160 °C using tetrabutylammonium iodide (2 mol%), conversion was 97.5% after 17 h and the ratio of products was only slightly altered for **2a**, **3a** and **5a** (88:9:3).

The reaction has been successfully applied to other 1,1-dihydroperfluorinated alcohols whose boiling points are 140 °C or higher, and the results are listed in Table 2. Curiously, trihydroperfluorinated alcohols required more forceful reaction conditions.

It was desirable to extend the reaction to lower boiling fluorinated alcohols. Imidazole and, to a lesser extent, tertiary aliphatic amines have been utilized to catalyze the hydroxyethylation of phenols using **4** [10]. Imidazole, however, when employed in either catalytic or stoichiometric amounts, provided poor conversions, e.g. 10–30% at 95 °C for 6 h, of the *O*-hydroxyethylated product **2e** of 1*H*,1*H*,3*H*-perfluoro-1-propanol (**1e**; b.p., 109–110 °C). Triethylamine, on the other hand, was a much more effective catalyst for promoting the *O*-hydroxyethylation. When added at the

TABLE 1

Effect of tetraalkylammonium iodides on the hydroxyethylation of 1,1-dihydroperfluorooctanol (1a)

Entry	Catalyst[b]	% Conversion[a] at reaction time			% By-products after 22 h
		1 h	6 h	22 h	
1	$Me_4N^+ I^{-c}$	18	61	87	9
2	$Et_4N^+ I^-$	18	59	90	8
3	$Pr_4N^+ I^-$	17	64	95	10
4	$Bu_4N^+ I^-$	17	56	93	7
5	$Bu_4N^+ I^{-d}$	–	–	84	5

[a] % Conversions were determined by ^1H NMR spectroscopy comparing the integrated areas of the newly-formed OCH_2CH_2 multiplets centered at *c.* 3.74 ppm to the R_FCH_2O resonances for starting and product alcohols centered at *c.* 4.04 ppm.

[b] Unless otherwise indicated, catalyst concentrations were 2 mol% based on **1a**, and **4** was employed at 1.50 equiv. relative to **1a**.

[c] A white solid formed in the period from 6–22 h.

[d] Reaction was conducted using 4 mol% catalyst and 1.25 equiv. of **4**.

TABLE 2

O-Hydroxyethylation of high-boiling 1,1-dihydroperfluorinated alcohols

Alcohol	Reaction conditions[a]		% Conversion[b]	% By-products[b]	% Isolated yield
	Temp. (°C)	Time (h)			
$H(CF_2)_4CH_2OH$ (**1b**) (b.p., 104–141 °C [12])	140	90	94	9	69
$H(CF_2)_8CH_2OH$ (**1c**) (b.p., 122–123 °C/52 Torr [11])	175	40[c]	95	18	39
$H(CF_2)_{10}CH_2OH$ (**1d**) (b.p., 180–181 °C/200 Torr [11])	150	80	100	15	69
$H(CF_2)_{10}CH_2OH$ (**1d**)	160	24	75	3	–

[a] Reactions were all conducted using 1.5 equiv. of **4** and tetrabutylammonium iodide (2 mol% based on alcohol) as catalyst.

[b] Conversions and by-product amounts were determined by GC or NMR methods.

[c] After 22 h, GC analysis showed very little **4** and 52% conversion; another 1.5 equiv. of **4** was added at this point.

0.5–1.0 equiv. level, 55–80% conversions of the propanol were observed under the same conditions with little or no by-product formation. Residual triethylamine was easily removed either by distillation or extraction into aqueous acid. Table 3 lists the results obtained on employing triethylamine catalysis to effect the *O*-hydroxyethylation of other 1,1-dihydroperfluorinated alcohols.

The reaction was unsuitable for 1,1-dihydroperfluorinated alcohols which possess a perfluoroalkyl substituent at position 2 and for secondary alcohols. No reaction was observed between **4** and 1,1-dihydroperfluorocyclohexylmethanol (**1i**) or 1,1,1,3,3,3-hexafluoro-2-propanol (**1j**), possibly for steric reasons.

Hydroxypropylation of 1,1-dihydroperfluorinated alcohols employing propylene carbonate was examined, but was found not to take place as readily as the reaction with **4**. With the use of quaternary ammonium salt catalysis, **1a** required more forceful reaction conditions, i.e. *c* 170 °C for 48 h, and larger quantities of the carbonate reagent, e.g. 4.5 equiv, to effect 80% conversion; no reaction was observed at 110 °C for 22 h using a full equivalent of triethylamine. The reaction was found to be highly regioselective ($>90\%$), in that nucleophilic attack principally occurred at the least-substituted carbon atom of propylene carbonate to afford the secondary alcohol product (**7**) in 45% isolated yield. Evidently under the more forceful reaction conditions necessary with propylene carbonate, propylene oxide and carbon dioxide formation effectively compete with hydroxypropylation.

TABLE 3

O-Hydroxyethylation of lower-boiling 1,1-dihydroperfluorinated alcohols[a]

Alcohol	Time (h)	% Conversion[b]	Alkylation products (mono/bis) ratio[c]	% Isolated yield
CF_3CH_2OH (**1e**) (b.p., 74–75 °C [12])	16	99	69:31	58
$CF_3CF_2CH_2OH$ (**1f**) (b.p., 80.6 °C [12])	16	86	87:13	71
$HCF_2CF_2CH_2OH$ (**1g**) (b.p., 109–110 °C [12])	16	94	89:11	67
$CF_3(CF_2)_2CH_2OH$ (**1h**) (b.p., 95–96.5 °C [12])	18	92	94:6	62
$H(CF_2)_4CH_2OH$ (**1b**) (b.p., 140–141 °C [12])	16	91	95:5	65
$CF_3(CF_2)_6CH_2OH$ (**1a**) (b.p., 146 °C [12])	28	91	94:6	66
$H(CF_2)_8CH_2OH$ (**1c**) (b.p., 122–123 °C/52 Torr [11])	100	80	95:5	–

[a] All reactions were conducted using 1.0 equiv. of triethylamine and 1.5 equiv. of **4** at 95 °C.

[b] % Conversions were determined by GC methods; thermal conductivity and flame ionization detectors provided conversion and product ratios agreeing within 3%.

[c] Ratios of desired mono (i.e. *O*-hydroxyethylated) to bis (i.e. *O*-hydroxyethoxyethylated) product.

Experimental

Materials and equipment

1,1-Dihydroperfluorinated alcohols were all commercial samples and were utilized without further purification. Sources for the alcohols included Aldrich Chemical Co. (Milwaukee, WI) [2,2,2-trifluoroethanol (**1e**)], Columbia Organic Chemical Co., Inc. (Gainesville, FL) [1*H*,1*H*-dihydroperfluoro-1-propanol (**1f**)], DuPont (Wilmington, DE) [1*H*,1*H*,3*H*-trihydroperfluoro-1-propanol (**1g**)], SCM (Gainesville, FL) [1*H*,1*H*-dihydroperfluoro-1-butanol (**1h**)], PCR (Gainesville, FL) [1,1,1,3,3,3-hexafluoro-2-propanol (**1j**), 1*H*,1*H*,5*H*-trihydroperfluoro-1-pentanol (**1b**) and 1*H*,1*H*,11*H*-trihydroperfluoro-1-undecanol (**1d**], 3M (St. Paul, MN) [1,1-dihydroperfluorooctanol (**1a**) and 1,1-dihydroperfluorocyclohexylmethanol (**1i**)] and Strem Chemicals. Inc. (Newburyport, MA) [1*H*,1*H*,9*H*-trihydroperfluoro-1-nonanol (**1c**]. Ethylene and propylene carbonates and the tetraalkylammonium iodides were obtained from Aldrich Chemical Co.

NMR spectra were obtained on a Varian XL-400 spectrometer operating at 400 and 101 MHz for ^{1}H and ^{13}C nuclei, respectively, using a 5-mm switchable carbon–hydrogen probe. All spectra were obtained using deuterochloroform solutions unless otherwise stated, and values are reported in ppm relative to a tetramethylsilane standard. COSY and heteronuclear correlation spectra were recorded using standard pulse sequences.

Gas chromatographic analyses were performed using either a Hewlett-Packard 5790 gas chromatograph equipped with a thermal conductivity detector and employing a 6 ft. × 1/8 in. stainless-steel column packed with UC W-98 (10%) on Chromosorb W (80–100 mesh) over a column temperature range of 75–275 °C (10 °C min^{-1}) or a Hewlett-Packard 5890 series II gas chromatograph equipped with a flame detector and employing a capillary column [HP-5 (30 m × 0.53 mm)] over a temperature range of 50–250 °C (10 °C min^{-1}). In no instance with the two detection systems was there a disparity of more than 3%. GC–MS was conducted using a Hewlett-Packard 5988 GC–MS instrument equipped with EI/CI sources. A capillary GC column (30 m × 0.25 mm) heated from 50–280 °C at 10 °C min^{-1} was employed for the analyses, and full scans from 60 to 1000 *m/z* were recorded.

Tetraalkylammonium iodide-catalyzed reactions

*1,1-Dihydroperfluorooctyl 2-hydroxyethyl ether (**2a**)*

In a 1 l round-bottomed flask equipped with a mechanical stirrer, thermometer and condenser/gas bubbler arrangement were charged 1,1-dihydroperfluorooctanol (**1a**) (400 g; 1 mol), ethylene carbonate (88 g; 1.5 mol) and tetramethylammonium iodide (7.38 g; 0.02 mol). The mixture of solids was warmed to *c*. 90 °C to achieve a homogeneous light brown solution. Warming was continued and the color of the reaction mixture lightened noticeably at 110 °C. At 115 °C, gas evolution was observed and the temperature was slowly raised to 140 °C over the next few hours so that gas evolution did not become uncontrollably fast. Carbon dioxide continued to bubble for about 48 h, at which point GC analysis (thermal conductivity detection) showed less than 5% starting alcohol (retention time, 3.2 min) remained, 86% of a higher boiling component (retention time, 7.2 min) and two lesser components comprising 6% (retention time, 10.7 min) and 8% (retention time, 16.3 min) of the mixture. The reaction solution was cooled and poured into a separatory funnel containing 1400 ml diethyl ether and 500 ml water. The upper organic layer was extracted with an additional 500 ml water and dried ($MgSO_4$). Removal of the ether at reduced pressure and vacuum fractional distillation of the residue provided the desired product (**2a**) (293.5 g; 66%), b.p. 65–66 °C/0.7 Torr (lit. value [11] 117–118 °C/20 Torr) and additional fractions that were enriched in the higher boiling side-products.

Characterization of the products of the reaction was as follows:

1,1-Dihydroperfluorooctyl 2-hydroxyethyl ether (**2a**): IR: 2.95 (OH) and broad absorptions from 8.0–8.7 (CF_2) μm; ^{1}H NMR δ: 3.25 (t, $J=5.5$ Hz, 1H); 3.73 (m, 4H); and 4.02 (t, $J=14$ Hz, 2H) ppm; and ^{13}C NMR (non-fluorine substituted carbons) δ: 61.6; 68.1; and 74.3 ppm. The minor product with a retention time of 10.7 min comprising 6% of the product mixture was identified as the bis(alkylated) product 1,1-dihydroperfluorooctyl 5-hydroxy-3-oxapentyl ether (3a) based on its NMR spectra from a mixture (36:64 of **2a**:**3a**) with **2a** [^{1}H NMR of **3a** δ: 3.62 (t, $J=4.8$ Hz, 2H); 3.68 (m, 2H); 3.75 (t, $J=4.8$ Hz, 2H); 3.8 (m, 2H); and 4.02 (t, $J=14$ Hz, 2H) ppm ^{13}C NMR (non-fluorine substituted carbon atoms) δ: 61.1; 67.7; 69.8; 72.0; and 72.2 ppm] and GC–MS (chemical ionization with methane) (P+1 at 489). The other minor product was identified as di-2-(1,1-dihydroperfluorooctyloxyethyl carbonate (**5a**) based on its IR spectrum (C=O at 5.70 μm), ^{1}H NMR spectrum [δ 3.87 (t, $J=4.6$ Hz, 4H); 4.02 (t, $J=13.8$ Hz, 4H); and 4.33 (t, $J=4.6$ Hz, 4H) ppm]; ^{13}C NMR spectrum [(non-fluorine substituted carbon atoms) δ 67.7; 68.4; 70.2; and 155.0 ppm] and GC–MS (chemical ionization with methane) in which a significant P+1 peak was observed at 915.

A reaction on the same scale with tetrabutylammonium iodide as the catalyst and at 160 °C for 17 h gave a conversion of 97.5%. The same products were obtained in a ratio of 88:9:3 for **2a**, **3a** and **5a**; the isolated yield of **2a** was 79%.

Other O-*hydroxyethylated compounds*

Employing the above procedure and the conditions specified in Table 2, the following *O*-hydroxyethylated compounds were prepared:

1,1,5-Trihydroperfluoropentyl 2-hydroxyethyl ether (**2b**): 69% yield; b.p., 103–106 °C/16 Torr (lit. value [11], 121–123 °C/40 Torr). ^{1}H NMR δ: 3.75 (m, 4H); 4.01 (t, $J=14$ Hz, 2H); and 6.08 (d of t, $J=52$ and 5.5 Hz, 1H) ppm. ^{13}C NMR (non-fluorine substituted carbon atoms) δ: 61.0; 67.4; and 73.8 ppm.

1,1,8-Trihydroperfluorononyl 2-hydroxyethyl ether (**2c**): 39% yield; b.p., 98 °C/1.25 Torr (lit. value [11], 131–133 °C/10 Torr). ^{1}H NMR δ: 3.74 (m, 4H); 4.03 (t, $J=14$ Hz, 2H); and 6.05 (d of t, $J=52$ and 5.3 Hz, 1H) ppm.

^{13}C NMR (non-fluorine substituted carbon atoms) δ: 61.4; 68.0; and 74.3 ppm.

1,1,11-Trihydroperfluoroundecyl 2-hydroxyethyl ether (**2d**): 69% yield; b.p., 140–143 °C/9 Torr (lit. value [11], 139–140 °C/9 Torr) which later crystallized to a white solid melting at 57–59 °C. ^1H NMR ($CDCl_3$/Freon 113) δ: 2.80 (m, 1H); 3.75 (m. 4H); 4.02 (t, $J = 14$ Hz, 2H); and 5.85–6.20 (m, 1H) ppm. ^{13}C NMR (non-fluorine substituted carbon atoms) δ: 61.7; 68.1; and 74.3 ppm.

1,1-Dihydroperfluorooctyl 2-hydroxy-2-methylethyl ether (**7**): A 250 ml round-bottomed flask equipped with a magnetic stirring bar and condenser/gas bubbler arrangement was charged with **1a** (63.83 g; 0.159 mol), propylene carbonate (24.4 g; 0.239 mol) and tetramethylammonium iodide (0.64 g; 0.0032 mol). The mixture was heated to 160 °C before any gas evolution was observed. After 24 h, gas evolution had ceased, but GC analysis indicated that only 45% conversion of the starting fluorinated alcohol had taken place. At this point another 40.5 g propylene carbonate was added, and the solution was heated at 170 °C for 24 h; the conversion at this point was 80%. The reaction mixture was worked-up as with the corresponding ethylene carbonate reaction. Fractional distillation provided 33.1 g of the title compound distilling at 80 °C/0.4 Torr (lit. value [1e], 78–86 °C/0.35 Torr). This quantity corresponded to an overall yield of 45% (or 57% based on converted starting alcohol). ^1H NMR δ: 1.17 (t, $J = 6.5$ Hz, 3H); 2.83 (d, $J = 3.5$ Hz, 1H); 3.45 (dd, $J = 9.5$ and 7.6 Hz, 1H); 3.61 (dd, $J = 9.5$ and 3.0 Hz, 1H); 4.0 (m, 1H); and 4.0 (t, $J = 13.5$ Hz, 2H) ppm. ^{13}C NMR (non-fluorine substituted carbon atoms) δ: 18.2; 66.3; 68.1; and 78.4 ppm. NMR analysis of the reaction mixture prior to distillation indicated that *c.* 10% of the mixture could not be assigned, although the primary alcohol regio isomer was not determined unambiguously as being present.

Triethylamine-catalyzed reactions

1,1-Dihydroperfluoroethyl 2-hydroxyethyl ether (2e)

A mixture of 2,2,2-trifluoroethanol (**1e**) (10.0 g; 0.100 mol), ethylene carbonate (13.2 g; 0.150 mol) and triethylamine (10.1 g; 0.100 mol) was stirred and warmed slowly to 95 °C. When the temperature reached *c.* 70 °C, the mixture became homogeneous. After 16 h at 95 °C, GC analysis indicated 99% conversion of starting alcohol. Distillation at atmospheric pressure provided 8.4 g (58% yield) of the desired product (b.p., 140 °C; lit. value [1a], 84 °C/70 Torr). ^1H NMR δ: 3.90 (q, $J = 8.8$ Hz, 2H); 3.75 (m, 4H); and 2.90 (s, 1H) ppm. ^{13}C NMR (non-fluorine substituted carbon atoms) δ: 61.3; 68.5; and 73.8 ppm.

Other O-hydroxyethylated compounds

Employing the above procedure and the conditions specified in Table 3, the following *O*-hydroxyethylated compounds were prepared:

1,1-Dihydroperfluoropropyl 2-hydroxyethyl ether (**2f**): 71% yield; b.p., 68–73 °C/29 Torr (lit. value [13], 87 °C/84 Torr). ^1H NMR δ: 2.88 (br s, 1H); 3.77 (m, 4H); and 4.01 (t, $J = 13.3$ Hz, 2H) ppm. ^{13}C NMR (non-fluorine substituted carbon atoms) δ: 61.4; 67.6; and 74.1 ppm.

1,1,3-Trihydroperfluoropropyl 2-hydroxyethyl ether (**2g**): 67% yield; b.p. 85–94 °C/16 Torr (lit. value [11], 178–179 °C). ^1H NMR δ: 5.98 (tt, $J = 53$ and 4.8 Hz, 1H); 3.89 (t, $J = 12.8$ Hz, 2H); 3.72 (m, 4H); and 3.20 (br s, 1H) ppm. ^{13}C NMR (non-fluorine substituted carbon atoms) δ: 61.2; 67.9; and 73.7 ppm.

1,1-Dihydroperfluorobutyl 2-hydroxyethyl ether (**2h**): 62% yield; b.p., 74–80 °C/22 Torr (lit. value [11], 160–161 °C). ^1H NMR δ: 2.86 (br s, 1H); 3,75 (m, 4H); and 4.01 (t, $J = 13.9$ Hz, 2H) ppm. ^{13}C NMR (non-fluorine substituted carbon atoms) δ: 61.4, 67.7; and 74.2 ppm.

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