Syntheses, Derivatives, Solubility, and Interfacial Properties of 2-Methyl-2-polyfluoroalkenyloxymethyl-1,3-propanediols: Potential Building Blocks for Syntheses of Amphiphatic Macromolecules†

Bamidele A. Omotowa, Matthew R. Judd, Brendan Twamley, and Jean'ne M. Shreeve*

Department of Chemistry, University of Idaho, Moscow, Idaho 83844-2343

jshreeve@uidaho.edu

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2-Hydroxymethyl-2-methyl-1,3-propanediol (**A**) was reacted with $(Me_3Si)_2NH$ and toluenesulfonyl chloride (TsCl) to give mainly $CH_3C(CH_2OSiMe_3)_3$ (**1**), and $CH_3C(CH_2OTs)_3$ (**2**), respectively. With allyl bromide, the products were $CH_3C(CH_2OCH_2CH{=}CH_2)_2(CH_2OH)$ (**3**) and $CH_3C(CH_2OCH_2CH{=}CH_2)(CH_2OH)_2{\cdot}H_2O$ (**4**). The reactions of **4** with perfluoroalkyl iodides (R_fI) were catalyzed by Cu(I)Cl to form 2-methyl-2-polyfluoroalkenyloxymethyl-1,3-propanediols: $(R_fCH{=}CHCH_2OCH_2)C(Me)(CH_2OH)_2$ [$R_f = C_4F_9$ (**5**), C_8F_{17} (**6**), and $(CF_2CF_2)_4OCF(CF_3)_2$ (**7**)]. Reduction of **5** and **6** with hydrogen gave two new 2-methyl-2-polyfluoroalkyloxymethyl-1,3-propanediols, **8** and **9**. The sodium salt of **9** was reacted with allyl bromide or acetyl chloride to form $(C_8F_{17}CH_2CH_2CH_2OCH_2)C(Me)(CH_2OX)(CH_2OH)_2$ [where $X = CH_2CH{=}CH_2$ (**10**) or $C(O)CH_3$ (**12**)] and $(C_8F_{17}CH_2CH_2CH_2OCH_2)C(Me)(CH_2OX)_2$ [where $X = CH_2CH{=}CH_2$ (**11**) or $C(O)CH_3$ (**13**)]. Reaction of tolenesulfonyl chloride with **7** gave the monotosylate, **14**, as the sole product. With 4-trifluoromethylbenzyl bromide, the sodium salt of **4** gave $(4\text{-}CF_3C_6H_4CH_2OCH_2)C(Me)(CH_2CH{=}CH_2)(CH_2OH){\cdot}H_2O$ (**15**). The compounds were characterized by NMR (^1H, ^{13}C, ^{19}F, ^{29}Si), GC-MS, and high-resolution MS or elemental analyses. UV evidence was obtained for partitioning of **9**, **12**, **14**, and **15** between perfluorodecalin and *n*-octanol. The test compounds acted as surfactants by facilitating the solubility of phenol and $Si(CH{=}CH_2)_4$ in perfluorodecalin. The single-crystal X-ray structure of **8** was also obtained. It crystallized in the monoclinic space group $P2_1/c$, and unit cell dimensions were $a = 24.966(2)$ Å ($\alpha = 90°$), $b = 6.1371(6)$ Å ($\beta = 100.730(2)°$), and $c = 10.5669(10)$ Å ($\gamma = 90°$).

Introduction

Perfluorochemicals have unique properties and are typically lipophilic and immiscible with some organic solvents.[1] However, polyfluorinated compounds containing functional groups such as −OH, NH_2, −COOH, −CHO, −COOR, C═O, etc. have increased solubility in water and other organic solvents.[2,3] Many polyfluorinated amphiphiles, with their unique properties and potential for applications as surfactants, coatings, adhesives, and drug delivery systems, are known.[3] However, asymmetric substitution of 2-(hydroxymethyl)-2-methyl-1,3-propanediol (**A**) will provide new routes to polyfluorinated compounds that can be starting materials in the synthesis of polymers with amphiphatic properties. As far as we know, there has been no previous use of **A** for this purpose. Part of our recent effort has been the investigation of useful new routes to prepare highly fluorinated compounds containing sites that could improve their solubility in organic solvents, perfluorochemicals, and possibly aqueous media. Now, we have found **A** to be a useful precursor to the 2-methyl-2-polyfluoroalkenyloxymethyl-1,3-propanediols. Reactions of either one or two OH groups in the polyfluoroalkyloxymethyl-1,3-propanediols yielded a number of compounds containing hydroxy, ester, allyl, and tosylate groups that influenced their solubility and, perhaps, their possible use as agents for interfacial transfer. Such derivatives could impact markedly the perfluorocarbon surfactant field. Although, the molecular structure of **A** was published,[4] no fluorinated derivatives of this compound were reported. Hence, we report the single-crystal X-ray structure of 2-methyl-2-(1′,1′,2′,2′,3′,3′,4′,4′-nonafluoroheptyloxymethyl)-1,3-propanediol, **8**.

Results and Discussion

Polyols are useful starting materials for the syntheses of polyfunctional compounds. Typical polyols such as pentaerythritol and glycerol have extensive hydrogen bonding networks that require high temperatures for reaction to occur[5] and make it difficult to control the degree of substitution.[6] Despite our efforts to direct the

* To whom correspondence should be addressed. Fax: 208-885-9146.

† Dedicated to Professor Dr. Dieter Naumann on the occasion of his 60th birthday.

(1) Hudlický, M., Pavlath, A. E., Eds.; In *Chemistry of Organic Fluorine Compounds II: A Critical Review*; ACS Monograph 187; American Chemical Society: Washington, DC, 1995; pp 985−988.

(2) (a) Yu, D.; Fréchet, J. M. J. *Polym. Mater. Sci. Eng.* **1998**, 633−634. (b) Milco, L. A.; Tomalia, D. A. U.S. Patent 5731095, March 24, 1998. (c) Cooper, A. I.; Londono, J. D.; Wignal. G.; McClain, J. B.; Samulski, E. T.; Lin, J. S.; Dobrynin, A.; Rubinstein, M.; Burke, A. L.; Fréchet, J. M. J.; DeSimone, J. M. *Nature* **1997**, *389*, 368−370.

(3) (a) Surfactant Virtual Library. http://www.surfactants.net/s-comp.htm (accessed Sept 2001). (b) Fréchet, J. M. J. *Science* **1994**, *263*, 1710. (c) Ungar, E. C. (to Imax Pharm. Corp.) U.S. Patent 6,028,066, February 22, 2000.

(4) Eilerman, D.; Lippman, R.; Rudman, R. *Acta Cryst.* **1983**, *B39*, 263−266.

(5) (a) Gordon, M.; Scantlebury, G. R. *J. Chem. Soc. B* **1967**, *1*, 1−13. (b) Yoshida, O.; Nagai, S. (to Mitsubishi Gas Chem. Co., Ltd., Japan), JP 2000044570, Feb. 15, 2000. (c) David, M. A.; Henry, G. S. In *Glycerol: A Jack of All Trades*; The Chemistry Hall of Fame, York University: 1996; and references therein.

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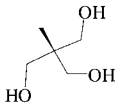
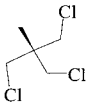
reaction on the basis of reactant stoichiometry, a variety of products were formed at elevated temperatures.[7] However, asymmetric substitution of the 2-(hydroxymethyl)-2-methyl-1,3-propanediol (**A**) and 2-(chloromethyl)-2-methyl-1,3-dichloropropane (**B**)[8] appeared to be possible via stepwise methodologies, thus making them likely intermediates for syntheses of our target polyfunctional compounds.



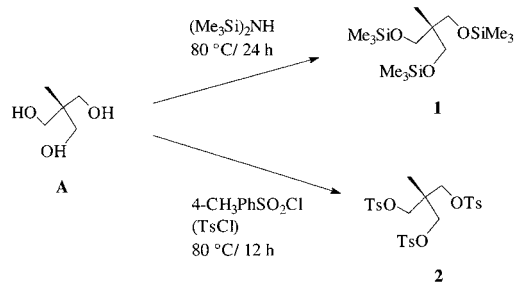
A



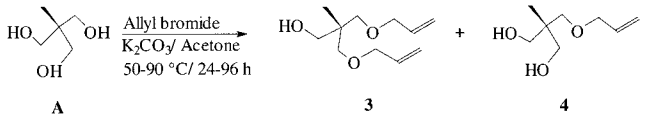
B

Although **B** reacted with allyl alcohol to give the allyl-substituted derivative,[8a] the probability existed that the chloride atoms might be involved in undesired reactions in subsequent steps required to prepare the polyfluoroalkenyloxymethyl derivatives. In principle, one of the terminal hydrogen atoms in the allyl substituent of $CH_2{=}CHCH_2OCH_2C(Me)(CH_2Cl)_2$ could react with a perfluoroalkyl iodide, R_fI, to produce $R_fCH{=}CHCH_2OCH_2$-$C(Me)(CH_2Cl)_2$-type compounds.[9,10] However, use of CuCl or Pd as part of the catalyst system in these procedures makes the chlorides very vulnerable at typical reaction temperatures.[10] Since our goal was to synthesize compounds that contained a polyfluoroalkyloxymethyl substituent and two other nonsimilar reactive sites, **B** was not a viable reactant.

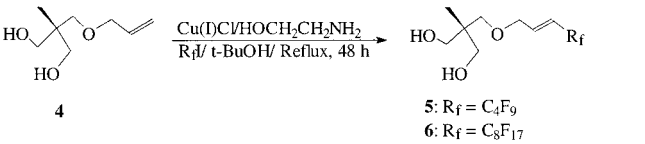
Given the stability of −OH groups in the presence of the CuCl catalyst system[9] and the opportunity for several low-temperature reactions that could lead to controlled substitution of $R_fCH{=}CHCH_2OCH_2C(Me)(CH_2OH)_2$-type compounds provided by the alcohol sites, **A** was the starting material of choice. It was reacted with a variety of reagents such as $(Me_3Si)_2NH$ and tosyl chloride (TsCl). Metathesis reactions did not occur at lower temperatures. Under these conditions, control of the number of substitutions was more difficult, and only tris(trimethylsilyloxymethyl)ethane (**1**) or tris(tosylatemethyl)ethane (**2**) was obtained as the major product. It was also difficult to control the degree of substitution in further reactions of **1** and **2**. For example, the reaction of **2** with sodium iodide in acetone gave a mixture of mono-, di-, and triiodo derivatives in low overall yields.



Compounds **3** and **4** were obtained from reaction of allyl bromide and **A**. They were purified either by distillation or by column chromatography (silica gel). With reduced hydrogen bonding in **4** (compared with **A**), the OH groups were more reactive at lower temperatures, especially with sodium hydride or pyridine.



The $CuCl/H_2NCH_2CH_2OH/t$-BuOH system[9] catalyzed the reactions of **4** and R_fI [R_f = C_4F_9, C_8F_{17}, and $(CF_2CF_2)_4OCF(CF_3)_2$] to give the respective 2-methyl-2-polyfluoroalkenyl-1,3-propanediols ($R_fCH{=}CHCH_2OCH_2$)-$C(Me)(CH_2OH)_2$ [$R_f = C_4F_9$ (**5**), C_8F_{17} (**6**), and $(CF_2CF_2)_4$-$OCF(CF_3)_2$ (**7**)] in high yields. They were purified either by distillation under reduced pressure or by column chromatography. Progress of these reactions was monitored by NMR (^1H and ^{19}F) and GC-MS. The peak area ratio changed from 2:1 for signals at ∼5.88 and 6.43 ppm assigned to CH_2 and CH in $CH{=}CH_2$, respectively, in the ^1H NMR spectrum of **4** to 1:1 in the spectra of **5**−**7**. The $^3J_{H-H}$ values of 14.88 (**5**), 15.25 (**6**), or 15.48 (**7**) Hz for the alkene proton signals appearing at 5.88 and 6.43 ppm in the ^1H NMR spectra of **5**−**7** indicate that they were isolated as the *E*-isomers.[11a] Also, the ^{19}F NMR signal for fluorine atoms of the ICF_2- moiety in R_fI [$R_f = C_4F_9$, C_8F_{17}, and $(CF_2CF_2)_4OCF(CF_3)_2$], typically observed at ca. −64 ppm, shifted to ca. −112 ppm (doublet with $^3J_{H-F}$ = 10.35 (**5**), 11.86 (**6**), or 12.41(**7**) Hz, respectively) in the spectra of **5**−**7**. The $CF_2CH{=}CH$ signals in the ^{13}C NMR spectra of **5**−**7** were observed as triplets ($^2J_{C-F}$ = 24 Hz) at about 117 ppm. The $[M + 1]^+$ ions were observed in the mass spectra of **5**−**7**. Compounds **6** and **7** are low-melting waxy solids, and **5** is crystalline.



Because of the reduced effect of hydrogen bonding, the hydroxy groups of **5**−**7** were more easily reacted than in **A**. The respective metal alkoxides were formed in reactions with sodium, potassium, sodium hydride, or potassium hydride at room temperature. In our hands, it was

(6) Ameduri, B.; Boutevin, B.; Karam, L. *J. Fluorine Chem.* **1993**, *65*, 43−47.

(7) Reaction of allyl bromide with pentaerythritol [$C(CH_2OH)_4$] produced a mixture of mono-, di-, and triallyl (in a ratio of 11:48:24 according to GC-MS) in the total crude yield of 1%. This result was reproduced in several attempts involving varying ratios of reactants and reaction temperatures and times.

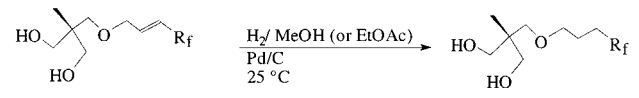
(8) (a) Müth, A.; Huttner, W. G.; Asam, A.; Zsolani, L.; Emmerrich, Ch. *J. Organomet. Chem.* **1994**, *468*, 149−163. (b) Ellermann, J.; Veit, A. *J. Organomet. Chem.* **1985**, *290*, 307−319. (c) Fukui, H.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1994**, *27*, 1297−1302. (d) Midollini, S.; Cecconi, F. *J. Chem. Soc., Dalton Trans.* **1973**, 681−683. (e) Burk, M. J.; Harlow, R. L. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1462−1464. (f) Jacobi, A.; Huttner, G.; Winterhalter, U.; Cunkis, S. *Eur. J. Inorg. Chem.* **1998**, 675−692.

(9) (a) Gaucheron, J.; Santaella, C.; Vierling, P. *Bioconjugate Chem.* **2001**, *12*, 114−128. (b) Burton, D. J.; Kehoe, L. J. *J. Org. Chem.* **1971**, *36*, 2596−2599. (c) Burton, D. J.; Kehoe, L. J. *J. Org. Chem.* **1971**, *35*, 1339−1342. (d) Asscher, M.; Vofsi, D. *J. Chem. Soc.* **1963**, 1887−1896. (e) Asscher, M.; Vofsi, D. *J. Chem. Soc.* **1963**, 3921−3927.

(10) (a) Elschenbroich, C.; Salzer, A. *Organometallics: A Concise Introduction*, 2nd ed.; VCH: Weinheim, Germany, 1992; p 419. (b) Jasperse, C. P.; Curron, D. P. *J. Am. Chem. Soc.* **1990**, *112*, 5601−5609. (c) Palladium catalyzes the coupling of aryl and alkenyl halides with alkenes: Masters, C. In *Homologous Transition-Metal Catalysis − A Gentle Art*; Chapman and Hall: New York, 1981; pp 1−37.

(11) (a) Pavia, D. L.; Lampman, G. M.; Kriz, G. S. In *Introduction to Spectroscopy*, 2nd ed.; Saunders College Publishing: 1996; pp 200−205. (b) Dobrovolna, Z.; Cerveny, L. *Collect. Czech. Chem. Comm.* **1997**, *62* (9), 1497−1502. (c) Anwer, M. K.; Sherman, D. B.; Roney, J. G.; Spatola, A. F. *J. Org. Chem.* **1989**, *54*, 1284−1289. (d) Hanson, R. W. *J. Chem. Educ.* **1997**, *74*, 430−431.

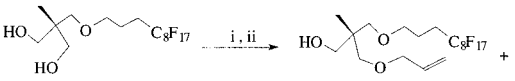
impossible to reduce **5**−**7** by using ammonium formate and Pd/C as an H_2-generator for similar hydrogenation reactions.[11b−d] However, the somewhat deactivated olefinic bonds in **5** and **6** were reduced via Pd/C-catalyzed hydrogenation in methanol or ethyl acetate to give **8** and **9**. These were stable, colorless or light yellow, low-melting solids. Because of the lower percentage of fluorine, it was possible to isolate **8** as a crystalline solid.



5-6

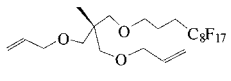
8: $R_f = C_4F_9$
9: $R_f = C_8F_{17}$

Reactions of the sodium salt of **9** with allyl bromide gave a mixture of **10** and **11**; reaction with acetyl chloride gave a mixture of **12** and **13**. These products were separated by chromatography (silica gel). Compounds **10**−**13** were stable, viscous, light yellow liquids.

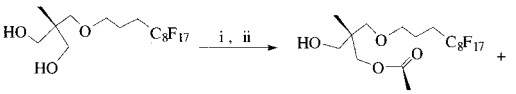


9 **10**

(i) NaH/ Et_2O/ 25 °C; (ii) allyl bromide

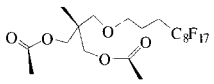


11



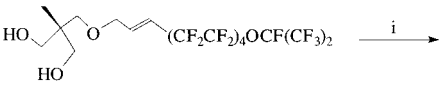
9 **12**

(i) NaH/ Et_2O/ 25 °C/ 2 h; (ii) $CH_3C(O)Cl$/ 45 °C/ 3 h



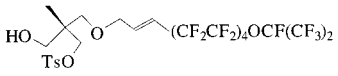
13

With TsCl, at temperatures between −5 and 5 °C,[6] **7** gave the monotosylate, **14**, as the only new compound. Disubstitution did not occur, which may arise from a combination of low-temperature and steric effects. However, this was fortunate since the goal was to retain one hydroxy group in the molecule.



7

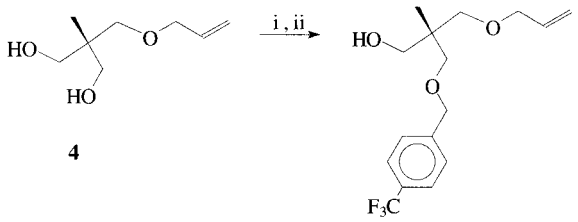
(i) TsCl/ Py/ -5 to 5 °C/ 2 h



14

Equimolar amounts of the sodium salt of **4** with 4-(trifluoromethyl)benzyl bromide led to **15**, which upon analysis was found to be the monohydrate.

In the syntheses of **11**, **12**, **14**, and **15**, low percentages of side products were often encountered. Mixtures of dichloromethane/methanol were very useful as eluents in column chromatography for separating pure samples



4 **15**

(i) NaH/ Et_2O/ 25 °C/ 2 h; (ii) 4-$CF_3C_6H_4CH_2Br$

of the desired product in high yields. This knowledge is useful for exploring other hydroxy-protective groups for selective reactions in our ongoing research. However, it was of interest to report on the solubility properties of **5**−**15**.

Solubility Studies. In addition to the synthetic challenge of synthesizing these amphiphatic compounds, we were also interested in the possibility of using **5**−**15** to develop new surfactants. The discovery of new surfactants that can facilitate the dissolution of nonfluorinated organic molecules in perfluorochemicals is still an active research area,[12] especially since they have assumed an increasing role in medical therapy.[13] Therefore, the solubilities of the **5**−**15** in different solvent media were examined.

Compound **A** is readily soluble in water, but, not unexpectedly, the substituted derivatives, **3** and **4**, were less soluble. The introduction of polyfluoroalkyl moieties in **5**−**9** resulted in a considerable reduction in their solubilities in water (assumed to be on the order of 1×10^{-4} M). They were insoluble in pentane, but were soluble in toluene, 1,1,2-trichlorotrifluoroethane (Freon-113), perfluorodecalin ($C_{10}F_{18}$), dichloromethane, and *n*-octanol.

Compounds **9**, **12**, **14**, and **15** were soluble in pentane, methylene chloride, toluene, perfluorodecalin, and Freon-113. Their solubilities in *n*-octanol are reported in Table 1. Compounds **11** and **13** that do not contain a hydroxy group were very soluble in most organic solvents, including hydrocarbons, such as pentane and hexane.

The high fluorine content (typically causing lipophilicity) and hydrogen-bonding possibilities (encouraging hydrophilicity) impact the solubility of these compounds in organic solvents. The dual-nature structures of **5**−**12**, **14**, and **15** would classify them as amphiphiles that could demonstrate interfacial activity.[2,3,14,15] The OH sites may be useful for ligation and may facilitate the solubilization of nonfluorinated compounds into perfluorochemicals in which they are normally not soluble. Therefore, we determined the extent of redistribution of **9**, **12**, **14**, and **15** from *n*-octanol into perfluorodecalin by UV spectrometry. The percent of these compounds that passed into the perfluorodecalin phase are reported in Table 1. The OH group in *n*-octanol forms hydrogen-bonding networks

(12) (a) Lehmler, H. J.; Bummer, P. M.; Jay, M. J. *CHEMTECH* **1999**, *29*, 7−13. (b) William, T. D.; Jay, M.; Lehmler, H.-J.; Clark, M. E.; Stalker, D. J.; Bummer, P. M. *J. Pharm. Sci.* **1998**, *87*, 1585−1589.

(13) (a) Lowe, K. C. *J. Fluorine Chem.* **2001**, *109*, 59−65 and references therein. (b) Lowe, K. C. In *Organofluorine Chemistry: Principles and Commercial Applications*; Banks, R. E., Smart, B. E., Tatlow, J. C., Eds.; Plenum Press; New York, 1994; Chapter 26, pp 555−577. (c) Leonard, R. C. *Anaesth. Intens. Care* **1998**, *26*, 11−21.

(14) (a) Dale, J.; Fredriksen, S. B. *Acta Chem. Scand.* **1992**, *46*, 278−282. (b) Thorne, C. M.; Rawle, S. C.; Adams, G. A.; Cooper, S. R. *Inorg. Chem.* **1986**, *25*, 3848−3850. (c) Cooper, S. R. (to ISIS Innovation, Ltd., UK) U.S. Patent 5621144, Apr 15, 1997.

(15) Richter, B.; de Wolf, E.; van Koten, G.; Deelman, B.-J. *J. Org. Chem.* **2000**, *65*, 3885−3893.

Table 1. Solubility and Percent of 9, 12, 14, and 15 Extracted from *n*-Octanol into Perfluorodecalin

compound	solubility (g/L)[a] in *n*-octanol	% interfacial transfer[b] [$P_{Fc/oct}$]
9	16.2	14.33
12	8.3	16.97
14	18.1	8.05
15	15.3	15.73

[a] Determined from a saturated solution at 25 °C. A correlation of UV absorbance to concentration on the standard Beer−Lambert plot. [b] From *n*-octanol into perfluorodecalin phase. Fc = perfluorodecalin.

with the hydroxy functionality(ities) in **9**, **12**, **14**, and **15**. Since bonding interactions with perfluorodecalin are essentially nonexistent, there was minimal transfer into the perfluorochemical phase.

In phenol, the hydroxy group can be used for hydrogen bond interactions, the aromatic ring is electron withdrawing and can interact with electron-rich functionalities by $\pi-\pi$ interaction. This donor−acceptor electronic property of phenol makes it possible for it to redistribute between two immiscible organic solvents.[12] Hence, it was one of our choices for study of the interfacial activities of **9**, **12**, **14**, and **15** between octanol and perfluorodecalin. In the other choice, tetravinylsilane, the polyolefins are electron rich and do not associate by hydrogen bonding, and its interactions would be expected to be limited to $\pi-\pi$ associations. Hence, **9** (containing two hydroxy groups), **12** (containing one hydroxy and one acetyl group), **14** (containing one hydroxy, one alkene, and one tosyl group), and **15** (containing one hydroxy and one trifluorophenyl group) were selected to represent compounds with different functional groups that will have different strength of bonding associations with either phenol or tetravinylsilane.

Both phenol and tetravinylsilane are insoluble in perfluorodecalin. When dilute solutions of phenol or tetravinylsilane in *n*-octanol were shaken thoroughly with perfluorodecalin, the resultant extractions into the latter were subsequently studied by UV and NMR spectroscopy. Results indicated that very little or none of the phenol or tetravinylsilane transferred into perfluorodecalin. However, in similar experiments, when the *n*-octanol contained small amounts of **9**, **12**, **14**, or **15**, the UV and ^{1}H NMR spectra of the perfluorodecalin phase showed that **9** and **15** facilitated the transfer of fractions of dissolved phenol from the alcohol into perfluorodecalin (Figure 1). Similarly, transfers of fractions of tetravinylsilane from *n*-octanol into perfluorodecalin (Figure 2) were facilitated by **12** and **14**. The amounts of either phenol or tetravinylsilane that transferred into perfluorodecalin were determined from standard Beer−Lambert plots.

Experimental Section

General. The solvents (THF and diethyl ether) were dried with sodium and distilled over a purple solution of benzophenone. A standard Schlenk line system was used for carrying out the reactions under dry nitrogen conditions. ^{1}H, ^{13}C or [^{13}C{F}], ^{19}F, and ^{29}Si{^{1}H} NMR spectra were recorded in $CDCl_3$ on a spectrometer operating at 200 (^{1}H), 50 (^{13}C), 188 (^{19}F), and 59 (^{29}Si) MHz. Chemical shifts are reported in parts per million relative to the appropriate standard, Me_4Si for ^{1}H and ^{13}C or $CFCl_3$ for ^{19}F NMR spectra. Mass spectra (EI or CI) were obtained on an electron impact 70 eV spectrometer, and high-resolution mass spectra were obtained using a suitable mass spectrometer. The UV spectroscopic studies were carried out using quartz curvettes, and the data were analyzed using usual software. Elemental analyses were performed commercially.

Syntheses. [$CH_3C(CH_2OSiMe_3)_3$] (1). This compound was obtained by heating 12 g (100 mmol) of 2-(hydroxymethyl)-2-methyl-1,3-propanediol and hexamethyldisilazane (16.2 g, 100 mmol) in 15 mL of toluene under anaerobic conditions at 80 °C for 24 h. The title compound was obtained from fractional distillation at 112 °C/1 mm. The yield was 33% on the basis of the amount of alcohol starting material. NMR ($CDCl_3$): ^{1}H, δ 0.05 (s, 27H, $-CH_3$), 0.76 (s, 3H CCH_3), 3.33 (s, 6H, CCH_2O-); ^{13}C, δ −0.6, 16.2, 42.0, 64.2; ^{29}Si, δ +17.7. MS [mass, species, intensity (%)]: 321, $(M - Me)^+$, 1; 291, $[M - 3(Me)]^+$, 0.5; 191, $[M - 2(Me_3Si)]^+$, 78; 73, $(Me_3Si)^+$, 100. Anal. Calcd. for $C_{14}H_{36}O_3Si_3$: C, 49.94; H, 10.62. Found: C, 49.71; H, 10.37.

[$CH_3C(CH_2OSO_2C_6H_4CH_3)_3$] (2)[14]. This compound was obtained by heating 12 g (100 mmol) of 2-(hydroxymethyl)-2-methyl-1,3-propanediol and TsCl (19.05 g, 100 mmoL) in 35 mL of tetrahydrofuran (THF) under anaerobic conditions at 80 °C for 12 h. The title compound was obtained by crystallizing the crude oily product from a 20:1 pentane/ethyl acetate mixture. The yield was 21% on the basis of the amount of alcohol starting material. NMR ($CDCl_3$): ^{1}H, δ 0.85 (s, 3H, $-CH_3C$), 2.42 (s, 9H, $-C_6H_4CH_3$), 3.82 (s, 6H, CH_3CCH_2O-), 7.29, 7.66 (dd, 12H, $-C_6H_4CH_3$); ^{13}C, δ 17.1, 21.7, 39.4, 69.7, 127.9, 130.1, 131.8, 145.4. MS [mass, species, intensity (%)]: 581, $(M - 1)^+$, 26; 427, $[M - O_2SC_6H_4CH_3]^+$, 14; 411, $[M - O_3SC_6H_4CH_3]^+$, 16; 172, $[HO_3SC_6H_4CH_3]^+$, 30; 154, Ts^-, 100, 91, $[C_6H_4CH_3]^+$, 94.

Synthesis of 2-(Hydroxymethyl)-2-methyl-1,3-bis(allyloxymethyl)propane [$CH_3C(CH_2OH)(CH_2OCH_2CH=CH_2)_2$] (3) and 2-(Allyloxymethyl)-2-methyl-1,3-bis(hydroxymethyl)propane Monohydrate [$CH_3C(CH_2OH)_2(CH_2OCH_2CH=CH_2)]\cdot H_2O$ (4). 2-(Hydroxymethyl)-2-methyl-1,3-propanediol (**A**) (20.25 g, 135 mmol), allyl bromide (16.35 g, 135 mmol), potassium carbonate (20.80 g, 150 mmol), and 20 mL of acetone were placed in a two-necked 500 mL flask connected via a condenser and a stopcock to a nitrogen gas inlet. The mixture was held at reflux at 120 °C for 36 h. After the mixture was cooled, 100 mL of toluene and 10 mL of water were added to the mixture, and stirring was continued for another 5 min. The phases were separated, and the organic phase was washed twice with 5 mL portions of water. The cloudy aqueous phase was mixed with 50 mL of toluene and the aqueous phase removed azeotropically over a Dean and Stark setup. The combined organic phases were filtered and dried over $MgSO_4$. The crude filtrate consisted of the three possible allyl substitution products. A fraction distilling at 115−118 °C/1 mm was confirmed by GC-MS as **4** (GC retention time = 7.99 min) and another distilling at 96−100 °C/1 mm was identified as **3** (GC retention time = 8.45 min) substituted products. Pure **4** (19.70 g, 73% yield) and **3** (4 g, 11.85%, on the basis of alcohol starting material) were obtained by column chromatography (silica gel) using successive elutions with (a) 98:2 CH_2Cl_2/MeOH and (c) 95:5 CH_2Cl_2/MeOH mixtures. When 2 equiv of allyl bromide was reacted with 1 equiv of **A** in similar reactions, the yields were 55% **3** and 20% **4**.

Analytical data for [$CH_3C(CH_2OH)(CH_2OCH_2CH=CH_2)_2$] (**3**). NMR ($CDCl_3$): ^{1}H, δ 0.73 (s, 3H, $-CH_3$), 3.46 (d, 2H, $-CH_2CH=CH_2$), 3.29 (d, 6H, CH_3CCH_2O-), 3.87 (t, 2H, OH), 3.85 (d, 2H, $CH_2CH=CH_2$), 5.07 (dd, 1H, $CH_2CH=CH_2$), 5.80 (m, 2H, $CH_2CH=CH_2$); ^{13}C, δ 17.4, 40.7, 67.3, 72.9, 75.0, 116.7 and 134.6. MS [mass, species, intensity (%)]: 201, $(M + 1)^+$, 0.3; 185, $(M - CH_3)^+$, 70; 41, $(CH_2=CHCH_2)^+$, 100. HRMS for $C_{11}H_{20}O_4$ $(M + 1)^+$ calcd 201.1491, found 201.1485.

Analytical data for [$CH_3C(CH_2OH)_2(CH_2OCH_2CH=CH_2)]\cdot H_2O$ (**4**). NMR ($CDCl_3$): ^{1}H, δ 0.73 (s, 3H, $-CH_3$), 3.46 (d, 2H, $-CH_2CH=CH_2$), 3.29 (d, 6H, CH_3CCH_2O-), 3.87 (t, 2H, OH), 3.85 (d, 2H, $CH_2CH=CH_2$), 5.07 (dd, 1H, $CH_2CH=CH_2$), 5.80 (m, 2H, $CH_2CH=CH_2$); ^{13}C, δ 17.4, 40.7, 67.3, 72.9, 75.0, 116.7 and 134.6. MS [mass, species, intensity (%)]: 161, $(M - OH)^+$, 0.3; 145, $(M - CH_3)^+$, 70; 41, $(CH_2=CHCH_2)^+$, 100. Anal. Calcd for $C_8H_{18}O_4$: C, 53.91; H, 10.18. Found: C, 53.99; H, 9.58.

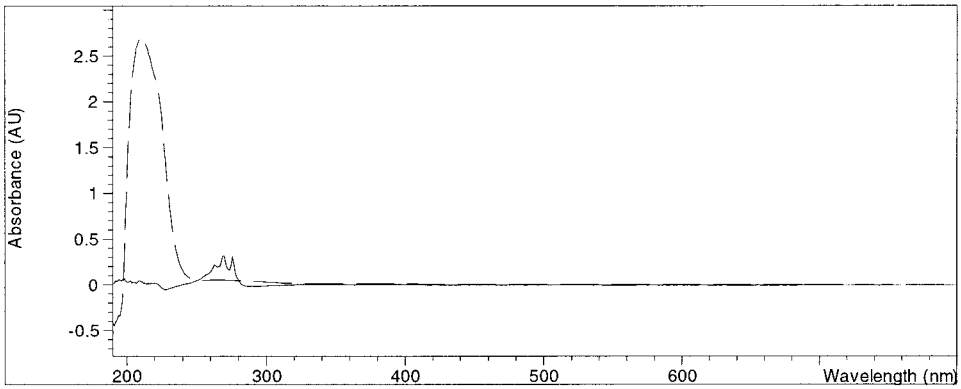


Figure 1. UV absorption curves for perfluorodecalin [(- - -): background] and solubilized phenol (−).

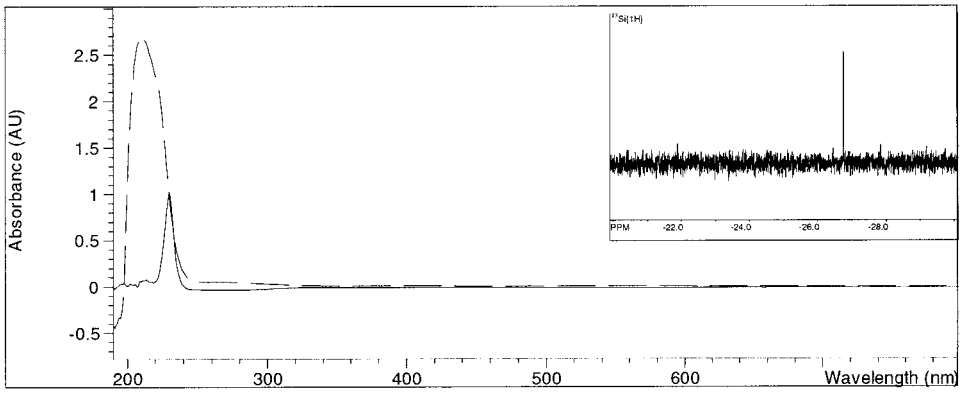


Figure 2. UV absorption curves for perfluorodecalin [(- - -): background] and solubilized tetravinylsilane (−). Inset: ^{29}Si NMR spectrum of tetravinylsilane in the perfluorodecalin phase.

Synthesis of $CH_3C[CH_2OCH_2CH{=}CHR_f][CH_2OH]_2$ [where $R_f = C_4F_9$ (5), C_8F_{17} (6), and $(CF_3)_2CFOCF_2CF_2)_4$ (7)]. A mixture of 0.99 g (6.19 mmol) of **4**, 4.22 g (7.74 mmol) of perfluorooctyl iodide, 0.40 g (4.04 mmol) of copper(I) chloride, 1.2 mL (19.88 mmol) of ethanolamine, and 6.0 mL (65.57 mmol) of *tert*-butyl alcohol was placed in a 100 mL two-necked flask connected with a reflux condenser and a nitrogen inlet via a two-way stopcock. The mixture was stirred at reflux at 80 °C for 48 h. On cooling, it was poured into a separating funnel that contain 50 mL of CH_2Cl_2 and 20 of mL water. The organic layer was separated and the aqueous phase washed twice with 15 mL portions of CH_2Cl_2. The combined organic phases were dried over magnesium sulfate and evaporated under reduced pressure to yield the crude product. GC-MS analysis indicated that the expected product, **6**, was 74% of the crude product that included two other products. Purification of **6** was achieved by repeated column chromatography (silica gel), eluting successively with 99:1 and 95:5 mixtures of CH_2Cl_2:CH_3OH. Compound **6** was a light yellow waxy solid (bp = 140 °C/1 mm). Yield = 2.5 g (70%).

Analytical data for $CH_3C[CH_2OCH_2CH{=}CHC_8F_{17}][CH_2OH]_2$ (**6**). NMR ($CDCl_3$): ^{1}H, δ 0.84 (s, 3H, $-CH_3$), 4.12 (d, 2H, $-CH_2$-CH=CH_2), 3.49 (s, 4H, CH_3CCH_2OH), 3.57 (s, 2H, CH_3CCH_2-OCH_2-), 2.15 (s, 2H, OH), 5.86 (td, 1H, $CH_2CH{=}CHC_8F_{17}$, $^3J_{H-H}$ = 15.25 Hz, $^3J_{H-F}$ = 11.86 Hz), 6.42 (dt, 1H, $CH_2CH{=}$ CHC_8F_{17}, $^3J_{H-H}$ = 15.25 Hz); ^{13}C, δ 16.9, 40.9, 67.6, 69.6, 75.2, 102.3−122.2, 117.2 (t, $^2J_{C-F}$ = 24 Hz), 138.8; ^{19}F, δ −81.0 (CF_3-$CF_2CF_2CF_2CF_2CF_2CF_2CH{=}CH$), −112.0 ($CF_3CF_2CF_2CF_2$-$CF_2CF_2CF_2CF_2CH{=}CH$, $^3J_{H-F}$ = 11.86 Hz), −122.9 (CF_3-$CF_2CF_2CF_2CF_2CF_2CF_2CF_2CH{=}CH$), −126.3 ($CF_3CF_2CF_2CF_2$-$CF_2CF_2CF_2CF_2CH{=}CH$). GC retention time: 9.9 min. MS [mass, species, intensity (%)]: 579, ($M^+ + 1$), 0.3; 219, $(CF_3$-$CF_2CF_2CF_2)^+$, 0.8; 169, $(CF_3CF_2CF_2)^+$, 2.8; 119, $(CF_3CF_2)^+$, 5; 57, $[CH_2CH(CH_3)_2]^+$, 100. Anal. Calcd. for $C_{16}H_{15}O_3F_{17}$: C, 33.23; H, 2.61; F, 55.85. Found: C, 33.15; H, 3.07; F, 54.63.

Analytical data for $CH_3C[CH_2OCH_2CH{=}CHC_4F_9][CH_2OH]_2$ (**5**). Yield = 43%. NMR ($CDCl_3$): ^{1}H, δ 0.79 (s, 3H, $-CH_3$), 4.07 (d, 2H, $-CH_2CH{=}CH_2$), 3.37 (s, 4H, CH_3CCH_2OH), 3.55 (s, 2H, $CH_3CCH_2OCH_2-$), 2.77 (s, 2H, OH), 5.78 (td, 1H, $CH^2CH{=}CHC_4F_9$, $^3J_{H-H}$ = 14.88 Hz, $^3J_{H-F}$ = 10.35 Hz), 6.38 (dt, 1H, $CH_2CH{=}CHC_8F_{17}$, $^3J_{H-F}$ = 14.88 Hz); ^{13}C, δ 17.3, 20.6, 40.8, 67.7, 69.8, 74.9, 104−118.6, 116.9 (t, $^2J_{C-F}$ = 24 Hz), 136.7; ^{19}F, δ −81.1 ($CF_3CF_2CF_2CF_2CH{=}CH$), −112.2 (CF_3CF_2-$CF_2CF_2CH{=}CH$, $^3J_{H-F}$ = 10.35 Hz), −123.2 ($CF_3CF_2CF_2CF_2$-$CH{=}CH$), −126.1 ($CF_3CF_2CF_2CF_2CH{=}CH$). GC retention time: 8.4 min. MS (EI) [mass, species, intensity (%)]: 379, (M^+ + 1), 14; 158, ($M^+ - C_4F_9H$), 45; 74, $[(CH_3)_3COH]^+$, 100. Rapid fragmentation (related to dehydration) of this compound made it difficult to record accurate mass for the M^+ ion of **5**. Hence, HRMS was obtained for the trimethylsilyl derivative of the two hydroxy groups, i.e., $C_4F_9CH{=}CHCH_2OCH_2C(CH_3)(CH_2$-$OSiMe_3)_2$ with expected m/z = 522. The $(M - 15)^+$ ion at m/z = 507 was stable enough for determination of accurate mass of this compound. HRMS for $C_{17}H_{28}O_3F_9Si_2$ $(M - 15)^+$ calcd 507.1433, found 507.1433.

Analytical data for $CH_3C[CH_2OCH_2CH{=}CH(CF_2CF_2)_4OCF$-$(CF_3)_2][CH_2OH]_2$ (**7**). Yield = 82%. NMR ($CDCl_3$): ^{1}H, δ 0.82 (s, 3H, $-CH_3$), 2.66 (s, 2H, OH), 3.48 (s, 2H, $CH_3CCH_2OCH_2-$), 3.65 (br, 4H, CH_3CCH_2OH), 4.13 (s, 2H, $CH_3CCH_2OCH_2$), 5.89 (td, 1H, $CH_2CH{=}CHC_8F_{17}$, $^3J_{H-H}$ = 15.48 Hz, $^3J_{H-F}$ = 12.41 Hz), 6.48 (d, 1H, $CH_2CH{=}CHC_8F_{17}$, $^3J_{H-H}$ = 15.48 Hz); ^{13}C, δ 16.9, 41.2, 67.8, 72.6, 75.9, 117.2 (t, J_{C-F} = 24 Hz), 138.8; ^{19}F, δ −81.1 ($(CF_3)_2CFOCF_2CF_2CF_2CF_2CF_2CF_2CF_2CH{=}CH$), −112.2 ($(CF_3)_2CFOCF_2CF_2CF_2CF_2CF_2CF_2CF_2CH{=}CH$, $^3J_{H-F}$ = 12.41 Hz), −122.5, −122.8, −123.9 ($(CF_3)_2CFOCF_2CF_2CF_2$-$CF_2CF_2CF_2CF_2CF_2CH{=}CH$), −125.8 ($(CF_3)_2CFOCF_2CF_2CF_2$-$CF_2CF_2CF_2CF_2CF_2CH{=}CH$), −145.7 ($(CF_3)_2CFOCF_2CF_2CF_2$-$CF_2CF_2CF_2CF_2CF_2CH{=}CH$). MS [mass, species, intensity (%)]: 745 ($M^+ + 1$), 100; 727 $(M - OH)^+$, 10; 709, $[R_fCH{=}CHCH_2$-$OCH_2C(CH_3)(CH{=}CH_2)]^+$*; 696, $[R_fCH{=}CHCH_2OCH_2C(CH_3)$-$(=CH_2)]^+$*, 8; 665, $[R_fCH{=}CHCH_2OCH_2]^+$*, 5; 527, $[R_fCH{=}CH$-$CH_3]^+$*, 5; 441, $[(CF_2)_8CH{=}CHCH_3]$, 6; 235, $[(CF_3)CFOCF_2]^+$, 7; 169, $[(CF_3)_2CF]^+$, 10; 158, $[CH_3C(CH_2OH)_2CH_2OCH_2CH{=}C]^+$, 9; 143, $[C(CH_2OH)_2CH_2OCH_2CH{=}C]^+$, 28; 129, $[C(CH_2OH)_2CH_2$-

$OCH{=}C]^+$, 12; 103, $[CH_3C(CH_2OH)_2(CH_2)]^+$, 15; 69, $(CF_3)^+$, 13; 57, $CH_3(CH_2)_3$, 48. Anal. Calcd for $C_{19}H_{15}O_4F_{23}$: C, 30.66; H, 2.03. Found: C, 31.84; H, 2.57. HRMS for $C_{19}H_{15}O_4F_{23}$ $(M + 1)^+$ calcd 745.0681, found 745.0673. $R_f = (CF_3)_2CFOCF_2CF_2CF_2CF_2CF_2CF_2CF_2$.

Synthesis of $CH_3C[CH_2OCH_2CH_2CH_2R_f][CH_2OH]_2$ [where $R_f = C_4F_9$ (8) or C_8F_{17} (9)]. Compounds **8** and **9** were obtained from reduction of **5** and **6** with H_2 gas in the presence of a suspension of 5% Pd/C in methanol or ethyl acetate.

Analytical data for $CH_3C[CH_2OCH_2CH_2CH_2C_4F_9][CH_2OH]_2$ (**8**). Yield = 99.9%. NMR ($CDCl_3$): ^1H, δ 0.74 (s, 3H, $-CH_3$), 1.79 (br, 2H, $C_4F_9CH_2CH_2CH_2O$), 2.07 (m, 2H, $C_4F_9CH_2CH_2CH_2O$), 3.42 (s, 2H, $C_4F_9CH_2CH_2CH_2O$), 3.37 (s, 4H, CH_3CCH_2OH), 3.57 (q, 2H, $CH_3CCH_2OCH_2-$), 3.29 (t, 2H, OH); ^{13}C, δ 17.3, 20.6, 27.8, 40.8, 67.7, 69.8, 74.9, 76.8, 104−118.6; ^{19}F, δ −81.1 ($CF_3CF_2CF_2CF_2CH_2CH_2$), −112.2 ($CF_3CF_2CF_2CF_2CH_2CH_2$), −123.2 ($CF_3CF_2CF_2CF_2CH_2CH_2$), −126.1 ($CF_3CF_2CF_2CF_2CH_2CH_2$). GC retention time: 8.9 min. MS [mass, species, intensity (%)]: 381, $(M + 1)^+$, 2; 363, $(M^+ - OH)^+$, 2; 72 $(CH_2OCH_2CH_2CH_2)^+$, 55; 57, $(OCH_2CH{=}CH_2)^+$, 100; 43, $(CH_2CH_2CH_3)^+$, 55. X-ray crystallographic data: crystal system, monoclinic; space group, $P2_1/c$; unit cell dimensions, $a = 24.966(2)$ Å ($\alpha = 90°$), $b = 6.1371(6)$ Å ($\beta = 100.730(2)°$), $c = 10.5669(10)$ Å ($\gamma = 90°$); $F(000) = 776$; crystal size = 0.26 × 0.10 × 0.05 mm^3; R1 (all data) = 0.1790, wR2 = 0.1670. Selected bond lengths (Å): F(1)−C(1) = 1.311(6), O(1)−C(8) = 1.419(5), C(1)−C(2) = 1.534(7). Selected bond angles (deg): C(7)−O(1)−C(8) = 111.8(3), C(3)−C(2)−C(1) = 116.4(5), O(1)−C(7)−C(6) = 109.0(4).

Analytical data for $CH_3C[CH_2OCH_2CH_2CH_2C_8F_{17}][CH_2OH]_2$ (**9**). Yield = 99.9%. NMR ($CDCl_3$): ^1H, δ 0.81 (s, 3H, $-CH_3$), 1.85 (m, 2H, $C_8F_{17}CH_2CH_2CH_2O$), 2.10 (m, 2H, $C_8F_{17}CH_2CH_2CH_2O$), 3.45 (s, 2H, $C_8F_{17}CH_2CH_2CH_2O$), 3.41 (s, 4H, CH_3CCH_2OH), 3.60 (q, 2H, $CH_3CCH_2OCH_2-$), 3.49 (t, 2H, OH); ^{13}C, δ 17.1, 20.6, 27.8, 40.7, 67.8, 70.1, 76.0, 77.0; ^{19}F, δ −81.0 ($CF_3CF_2CF_2CF_2CF_2CF_2CF_2CH_2CH_2$), −112.0 ($CF_3CF_2CF_2CF_2CF_2CF_2CF_2CH_2CH_2$), −122.9 ($CF_3CF_2CF_2CF_2CF_2CF_2CF_2CH_2CH_2$), −126.3 ($CF_3CF_2CF_2CF_2CF_2CF_2CF_2CH_2CH_2$). GC retention time: 10.1 min. MS [mass, species, intensity (%)]: 581, $(M + 1)^+$, 0.3; 563, $(M - OH)^+$, 0.6; 71, $[CH_2C(CH_3)_3]^+$, 58; 56, $[CH_2C(CH_3)_2]^+$, 100; 43, $[CH_2CH_2CH_3]^+$, 40. Anal. Calcd for $C_{16}H_{17}O_3F_{17}$: C, 33.12; H, 2.95; F, 55.66. Found: C, 32.26; H, 2.63; F, 54.54.

Synthesis of $CH_3C[CH_2OCH_2CH_2CH_2C_8F_{17}][CH_2OX][CH_2OH]$ [where X = $CH_2CH{=}CH_2$ (10), $C(O)CH_3$ (12)] and $CH_3C[CH_2OCH_2CH_2CH_2C_8F_{17}][CH_2OX]_2$ [where X = $CH_2CH{=}CH_2$ (11), $C(O)CH_3$ (13)]. The procedures for the syntheses and isolation of **10**−**13** were essentially the same. A mixture of 4 g (25 mmol) of **9** and 25 mL of THF and magnetic stir-bar were placed in a two-necked 250 mL flask connected with a stopcock to a nitrogen/vacuum inlet valve. Under anaerobic conditions, sodium hydride (0.6 g, 25 mmol) and 30 mL of diethyl ether were placed in a second flask. The suspension of sodium hydride was slowly transferred to the stirring solution of **9** under nitrogen. After the mixture was stirred for 2 h at room temperature, a solution of 2.2 g (28.03 mmol) of acetyl chloride in 20 mL of diethyl ether was added. A reflux condenser was connected to the flask and the reaction temperature raised to 40 °C. Aliquots were evaluated by GC-MS to establish the progress of the reaction. After 4 h, both $CH_3C[CH_2OCH_2CH_2CH_2C_8F_{17}][CH_2OCH_2CH{=}CH_2][CH_2OH]$ (**10**) and $CH_3C[CH_2OCH_2CH_2CH_2C_8F_{17}][CH_2OCH_2CH{=}CH_2]_2$ (**11**) were formed and separated by column chromatography (silica gel) by using 100% CH_2Cl_2, 98:2 CH_2Cl_2/MeOH, and 100% MeOH as eluents, in succession. The retention times for **10** and **11** from the GC-chromatogram were 10.1 and 11.5 min, respectively.

Analytical data for $CH_3C[CH_2OCH_2CH_2CH_2C_8F_{17}][CH_2OCH_2CH{=}CH_2][CH_2OH]$ (**10**). Yield = 56%. NMR ($CDCl_3$): ^1H, δ 0.80 (s, 3H, $-CH_3$), 1.86 (m, 2H, $CH_2CH_2C_8F_{17}$), 2.17 (m, 2H, $CH_2C_8F_{17}$), 2.91 (s, 1H, CH_2OH), 3.61 (s, 2H, CH_3CCH_2OH), 3.54 (s, 2H, $CH_2OCH_2CH_2CH_2C_8F_{17}$), 3.37 (s, 2H, $CH_2OCH_2CH{=}CH_2$), 3.93 (d, 2H, $CH_2CH{=}CH_2$), 5.85 (m, 1H, $CH_2CH{=}CH_2$), 5.17 (t, 2H, $CH_2CH{=}CH_2$); ^{13}C, δ 17.1, 20.6, 27.8, 40.7, 67.8, 69.2, 70.1, 76.0, 77.0, 116.6, 134.2; ^{19}F, δ −81.0 ($CF_3CF_2CF_2CF_2CF_2CF_2CF_2CF_2CH_2CH_2$), −112.0 ($CF_3CF_2CF_2CF_2CF_2CF_2CF_2CF_2CH_2CH_2$), −122.9 ($CF_3CF_2CF_2CF_2CF_2CF_2CF_2CF_2CH_2CH_2$), −126.3 ($CF_3CF_2CF_2CF_2CF_2CF_2CF_2CF_2CH_2CH_2$). MS [mass, species, intensity (%)]: 621, $(M + 1)^+$, 0.7; 563, $(M - OCH_2CH{=}CH_2)^+$, 2; 71, $(CH_2OCH_2CH{=}CH_2)^+$, 55; 57, $(OCH_2CH{=}CH_2)^+$, 45; 41, $(CH_2CH{=}CH_2)^+$, 100. HRMS for $C_{19}H_{22}O_3F_{17}$ $(M + 1)^+$ calcd 621.1299, found 621.1299.

Analytical data for $CH_3C[CH_2OCH_2CH_2CH_2C_8F_{17}][CH_2OCH_2CH{=}CH_2]_2$ (**11**). Yield = 18%, on the basis of the amount of alcohol starting material. NMR ($CDCl_3$): ^1H, δ 0.83 (s, 3H, $-CH_3$), 1.86 (m, 2H, $CH_2CH_2C_8F_{17}$), 2.17 (m, 2H, $CH_2C_8F_{17}$), 3.55 (s, 2H, CH_3CCH_2OH), 3.51 (s, 2H, $CH_2OCH_2CH_2CH_2C_8F_{17}$), 3.33 (s, 2H, $CH_2OCH_2CH{=}CH_2$), 3.93 (d, 2H, $CH_2CH{=}CH_2$), 5.85 (m, 1H, $CH_2CH{=}CH_2$), 5.17 (t, 2H, $CH_2CH{=}CH_2$); ^{13}C, δ 17.1, 20.6, 27.8, 40.7, 67.8, 69.2, 70.1, 76.0, 77.0, 116.6, 134.2; ^{19}F, δ −81.0 ($CF_3CF_2CF_2CF_2CF_2CF_2CF_2CF_2CH_2CH_2$), −112.0 ($CF_3CF_2CF_2CF_2CF_2CF_2CF_2CF_2CH_2CH_2$), −122.9 ($CF_3CF_2CF_2CF_2CF_2CF_2CF_2CF_2CH_2CH_2$), −126.3 ($CF_3CF_2CF_2CF_2CF_2CF_2CF_2CF_2CH_2CH_2$). MS [mass, species, intensity (%)]: 661, $(M + 1)^+$, 0.7; 591, $(M - CF_3)^+$, 2; 169, $(CF_2CF_2CF_3)^+$, 3; 71, $(CH_2OCH_2CH{=}CH_2)^+$, 54; 57, $(OCH_2CH{=}CH_2)^+$, 52; 41, $(CH_2CH{=}CH_2)^+$, 100. HRMS for $C_{22}H_{26}O_3F_{17}$ $(M + 1)^+$ calcd 661.1611, found 661.1624.

Analytical data for $CH_3C[CH_2OCH_2CH_2CH_2C_8F_{17}][CH_2OCOCH_3][CH_2OH]$ (**12**). Yield = 77%. NMR ($CDCl_3$): ^1H, δ 0.87 (s, 3H, $-CCH_3$), 2.03 (s, 2H, $CH_3C(O)OCH_2$), 3.26 (s, 2H, CH_3CCH_2OH), 3.46 (s, 2H, $CH_2OCH_2O(O)CCH_3$), 2.69 (br, 1H, OH), 3.99 (s, 2H, $CH_2OCH_2CH_2CH_2C_8F_{17}$), 4.05 (s, 2H, $CH_2OCH_2CH_2CH_2C_8F_{17}$), 1.86 (m, 2H, $CH_2OCH_2CH_2CH_2C_8F_{17}$), 2.12 (m, 2H, $CH_2OCH_2CH_2CH_2C_8F_{17}$); ^{13}C, δ 15.3, 17.0, 20.8, 27.9, 66.5, 69.9, 74.9, 171.5; ^{19}F, δ −81.0 ($CF_3CF_2CF_2CF_2CF_2CF_2CF_2CF_2CH_2CH_2$), −112.0 ($CF_3CF_2CF_2CF_2CF_2CF_2CF_2CF_2CH_2CH_2$), −122.9 ($CF_3CF_2CF_2CF_2CF_2CF_2CF_2CF_2CH_2CH_2$), −126.3 ($CF_3CF_2CF_2CF_2CF_2CF_2CF_2CF_2CH_2CH_2$). MS [mass, species, intensity (%)]: 623, $(M + 1)^+$, 0.4; 605, $(M - OH)^+$, 1; 72, $(CH_2OCH_2CH_2CH_2)^+$; 57, $(OCH_2CH{=}CH_2)^+$, 25; 43, $(CH_3CO)^+$, 100. Anal. Calcd for $C_{18}H_{19}O_4F_{17}$: C, 34.73; H, 3.06. Found: C, 35.25; H, 2.85.

Analytical data for $CH_3C[CH_2OCH_2CH_2CH_2C_8F_{17}][CH_2OCOCH_3]_2$ (**13**). Yield = 8.5%, on the basis of the amount of alcohol starting material. NMR ($CDCl_3$): ^1H, δ 0.87 (s, 3H, $-CCH_3$), 2.02 (s, 2H, $CH_3C(O)OCH_2$), 3.46 (s, 2H, $CH_2OCH_2O(O)CCH_3$), 3.99 (s, 2H, $CH_2OCH_2CH_2CH_2C_8F_{17}$), 4.05 (s, 2H, $CH_2OCH_2CH_2CH_2C_8F_{17}$), 1.86 (m, 2H, $CH_2OCH_2CH_2CH_2C_8F_{17}$), 2.12 (m, 2H, $CH_2OCH_2CH_2CH_2C_8F_{17}$); ^{13}C, δ 15.3, 17.0, 20.8, 27.9, 66.5, 69.9, 74.9, 171.5; ^{19}F, δ −81.0 ($CF_3CF_2CF_2CF_2CF_2CF_2CF_2CF_2CH_2CH_2$), −112.0 ($CF_3CF_2CF_2CF_2CF_2CF_2CF_2CF_2CH_2CH_2$), −122.9 ($CF_3CF_2CF_2CF_2CF_2CF_2CF_2CF_2CH_2CH_2$), −126.3 ($CF_3CF_2CF_2CF_2CF_2CF_2CF_2CF_2CH_2CH_2$). MS [mass, species, intensity (%)]: 665, $(M + 1)^+$, 0.5; 647, $(M - OH)^+$, 1; 72, $(CH_2OCH_2CH_2CH_2)^+$; 57, $(OCH_2CH{=}CH_2)^+$, 25; 43, $(CH_3CO)^+$, 100. HRMS for $C_{20}H_{22}O_5F_{17}$ $(M + 1)^+$ calcd 665.1196, found 665: 1201.

Synthesis of $CH_3C(CH_2OH)(CH_2OSO_2C_6H_4CH_3)[CH_2OCH_2CH{=}CH(CF_2CF_2)_4OCF(CF_3)_2]$ (14). This compound was prepared by a modification of the literature procedure.[16] *p*-Toluenesulfonyl chloride (0.21 g, 1.1 mmol) was added to **7** (1 g, mmol) in 10 mL of dry pyridine at −5 °C. The mixture was agitated until the chloride dissolved. Stirring was continued at 0 °C for an additional 2 h. The mixture was then carefully treated with 0.1, 0.1, 0.1, 0.2, and 0.5 mL of water at not more than 5 °C, with each addition spread over 5 min. Finally, 10 mL of water was then added at −5 °C. The toluenesulfonate was extracted with diethyl ether. The ether solution was washed with ice-cold dilute sulfuric acid, water, and sodium bicarbonate solution. It was dried over sodium sulfate and filtered and the solvent removed under reduced pressure. The crude product (**14**) was a light yellow liquid and was purified by elution from a silica gel column by using dichloromethane. No evidence for the disulfonated product was found, and any unreacted **7** was eventually washed down with methanol.

(16) Weygand, C. In *Preparative Organic Chemistry*, 4th ed.; Higetag, G., Martini, A., Eds.; Wiley: New York, 1972; pp 229−230.

Table 2. Amounts of Phenol and Tetravinylsilane Transferred from *n*-Octanol into Perfluorodecalin

		mmols transferred from *n*-octanol into perfluorodecalin[b]	
compounds	MW[a]	phenol	tetravinylsilane
9	580	0.0278	
12	623		0.0135
14	898		0.0125
15	336	0.0704	

[a] MW = molecular weight. [b] Original solutions before adding perfluorodecalin consisted of: 0.2 g (2.128 mmol) of phenol/2 mL of *n*-octanol/0.07 g of test compound (**9** or **15**) or 0.15 g (1.101 mmol) of tetravinylsilane/2 mL of *n*-octanol/0.07 g of test compound (**12** or **14**). See Experimental Section for method for determination of amounts in interfacial transfer.

Analytical data for $CH_3C(CH_2OH)(CH_2OSO_2C_6H_4CH_3)[CH_2OCH_2CH{=}CH(CF_2CF_2)_4OCF(CF_3)_2]$ (**14**). Yield = 0.95 g, 79%. NMR ($CDCl_3$): ^{1}H, δ 0.84 [s, 3H, CCH_3, 2.30 (s, 1H, CH_2OH), 2.39 (s, 3H, $C_6H_4CH_3$), 3.33 (s, 2H, CH_3CCH_2OH), 3.46 (s, 2H, $CH_3CCH_2OCH_2CH{=}CH$), 3.99 (d, 2H, $CH_3CCH_2OCH_2CH{=}CH$), 4.03 (s, 2H, $CH_3CCH_2OSO_2C_6H_4CH_3$), 5.73 [dt, 1H, $CH_2CH{=}CH(CF_2CF_2)_4OCF(CF_3)_2$], 6.28 [d, 2H, $CH_2CH{=}CH(CF_2CF_2)_4OCF(CF_3)_2$]; ^{13}C, δ 16.6, 21.5, 40.9, 65.9, 69.5, 72.1, 73.7, 117.3, 128.0, 129.9, 132.7, 145.0, 158.7; ^{19}F, δ −81.3 ($CF_3CF_2CF_2CF_2CF_2CF_2CF_2CH{=}CH$), −112.1 ($CF_3CF_2CF_2CF_2CF_2CF_2CF_2CH{=}CH$), −122.5, −122. 8, −123.9 ($CF_3CF_2CF_2CF_2CF_2CF_2CH{=}CH$), −125.8 ($CF_3CF_2CF_2CF_2CF_2CF_2CH{=}CH$). Anal. Calcd for $C_{26}H_{21}O_6SF_{23}$: C, 34.74; H, 2.34. Found: C, 35.34; H, 1.95.

Synthesis of $CH_3C[CH_2OCH_2C_6H_4CF_3][CH_2OH][CH_2OCH_2CH{=}CH_2]\cdot H_2O$ (15). A mixture of 0.5 g (3.13 mmoL) of **4** and 10 mL of freshly distilled diethyl ether and a magnetic stir bar were placed in a two-necked 50 mL flask connected via a stopcock to a nitrogen/vacuum inlet valve. A suspension of sodium hydride (0.075 g, 3.125 mmol) in 15 mL of diethyl ether was made up in a second flask under nitrogen. This was added to the stirring solution of **4** at 0 °C and slowly warmed to 25 °C. A solution of 0.75 g (3.125 mmol) of 4-trifluoromethylbenzyl bromide in 15 mL of THF was added to the mixture at 25 °C. After the mixture was stirred at this temperature for 1 h, the flask was equipped with a reflux condenser and the mixture heated at 40 °C for 3 h. After the mixture was cooled, the solvents were evaporated under reduced pressure. GC-MS analysis showed that the crude product was a mixture of unreacted **4** (6%), mono-(**15**) (80%), and dibenzyl compounds (5%), along with other side products. The benzylated compounds were separated from **4** by extracting the evaporated crude mixture with hexane. Compound **15** was obtained pure by repeated column chromatography using pentane/hexane mixtures. The GC retention time of **15** was 11.1 min. Analytical data for $CH_3C[CH_2OCH_2C_6H_4CF_3][CH_2OCH_2CH{=}CH_2]\cdot H_2O$ (**15**). Yield = 73%. NMR ($CDCl_3$): ^{1}H, δ 0.88 (s, 3H, CCH_3), 2.75 (br, 1H, OH), 2.75, 3.41 (, 2H, CH_2OH), 3.48 (s, 2H, $CH_3CCH_2OCH_2C_6H_4CF_3$), 3.57 (s, 2H, $CH_2OCH_2CH{=}CH_2$), 4.55 (s, 2H, $CH_3CCH_2OCH_2C_6H_4CF_3$), 3.95 (td, 2H, $CH_2OCH_2CH{=}CH_2$), 5.26 (dd, 2H, $CH_2OCH_2CH{=}CH_2$), 5.80 (m, 1H, $CH_2OCH_2CH{=}CH_2$), 7.37, 7.55 (dd, 4H, $CH_2C_6H_4CF_3$); ^{13}C, δ 17.2, 40.7, 68.1, 69.2, 72.5, 74.7, 116.9, 125.3, 125.4, 127.4, 134.6; ^{19}F, δ −62.7. MS [mass, species, intensity (%)]: 319, $(M+1)^+$, 277, $(M - CH_2CH{=}CH_2)^+$, 2; 159, $(M - CF_3C_6H_4CH_2)^+$ or $(CF_3C_6H_4CH_2)^+$, 100; 41, $(CH_2CH{=}CH_2)^+$, 40. Anal. Calcd for $C_{16}H_{23}O_4F_3$: C, 57.13; H, 6.89. Found: C, 56.91; H, 6.69.

Solution Studies. (i) Determination of Solubility of Test Compounds. Four different concentrations were made for each of **9**, **11**, **14**, and **15** in *n*-octanol. Their UV absorbance maxima at 213 (**9**), 232 (**11**), or 234 nm (**14** and **15**) were plotted to obtain the Beer−Lambert standard curve for each compound. Concentrations correlating the UV absorbancies (in the standard curves) of saturated solutions of **9**, **11**, **14**, and **15** were reported as their solubility in g/L (Table 1).

(ii) Determination of Partition Coefficient of the Test Compounds Between *n*-Octanol and Perfluorodecalin. The redistribution of each of these compounds from *n*-octanol into perfluorodecalin, reported as $P_{Fc/oct}$ in Table 1, was determined as follows: 2.0 mL of perfluorodecalin was added to a solution of a known concentration of the test compound in 2.0 mL of *n*-octanol, and the mixture was shaken thoroughly and allowed to settle and separate into two clear, colorless, immiscible phases. The *n*-octanol phase (top layer) was the carefully separated. The concentration of the compound that remained in the *n*-octanol phase was determined from the standard curve. These concentrations were used to calculate $P_{Fc/oct}$ according to the following equation:

$$P_{Fc/oct} = \frac{(\text{initial} - \text{final}) \text{ concentration of compound in } n\text{-octanol}}{\text{initial concentration of compound in } n\text{-octanol}} \times 100$$

(iii) Solubilization of Phenol and Tetravinylsilane in Perfluorodecalin. The solubilization of phenol and tetravinylsilane were evaluated as follows: 0.2 g of either phenol or tetravinylsilane was added to a 0.07 g of a solution of **9**, **11**, **14**, or **15** in 2.0 mL of *n*-octanol and shaken thoroughly for a minute. Perfluorodecalin (2 mL) was added to the homogeneous *n*-octanol solution and the final mixture shaken vigorously for another 1−2 min. When the mixture was allowed to settle, phase separation occurred. The NMR and UV spectra of the perfluorodecalin phases in the different experiments were recorded. Determinations of quantitative amounts of phenol and tetravinylsilane solubilized in perfluorodecalin were calculated as the difference between the initial and final concentrations in *n*-octanol, and using the equation in section ii above. The data are reported in Table 2.

Conclusion

The syntheses of new multifunctional and highly polyfluorinated compounds were achieved via high-yielding multistep procedures. Some of the compounds will be valuable starting materials in further syntheses and applications. Our investigation of their solubility and some of their interfacial properties revealed that they are soluble in many organic solvents and in perfluorodecalin. They were transferred from *n*-octanol into perfluorodecalin, and they also facilitated the solubilization of phenol and tetravinylsilane into the perfluorochemical via a similar transfer from octanol. The results indicate that the composition of the new compounds provides a useful basis on which to develop new surfactants for applications in perfluorochemicals. Since perfluorochemicals are gaining increasing significance as blood substitutes, liquid ventillators, etc., we anticipate that this contribution will lead to development of new useful surfactants.

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Supporting Information Available: Tables of data collection parameters, atom coordinates, bond distances and angles, anisotropic thermal parameters, hydrogen coordinates, and intermolecular hydrogen bonding. This material is available free of charge via the Internet at http://pubs.acs.org.

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