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AMINE(POLYFLUOROALKOXYACYL)IMIDE SURFACTANTS [1]

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SUMMARY

Twenty-one examples (**10a-d**, **11a-l** and **12a-e**) of a new class of surfactants, the amine(polyfluoroalkoxyacyl)imides, were prepared by the reaction of esters containing polyfluoroalkoxy groups with tertiary alkylaminimides and hydroxyalkylaminimides. Included are five examples of difunctional aminacylimides that contain the hydrophilic portion of the molecule in the middle. These new surfactants are among the most potent known in their ability to form aqueous solutions with very low surface tensions and can be used to prepare stable emulsions of perfluorodecalin in water. Two new esters (ethyl perfluorooctyloxyacetate, **7**, and ethyl 1*H*,1*H*-perfluorooctyloxyacetate, **9**) used as intermediates to the surfactants were prepared by the alkylation of perfluoro- and 1*H*,1*H*-perfluorooctanol salts with ethyl bromoacetate. Other esters used in the preparation of the surfactants were derived from oligomers of hexafluoropropene oxide.

INTRODUCTION

Surfactants that contain a polyfluoroalkyl group as the hydrophobic portion of the molecule are very potent in their ability to form aqueous solutions with very low surface tensions when compared with their fluorine-free analogs [2]. Inner salt surfactants such as aminacylimides are also very potent, in part because of their ability to form a closely packed monolayer at the water-air interface [3]. It is not surprising, therefore, that aminimide surfactants that contain polyfluoroalkyl groups as their hydrophobic portion are among the most potent surfactants known [4].

Biocompatible (non-toxic) surfactants could have a variety of medical uses, including use as an emulsifying agent in the preparation of a fluorocarbon artificial blood. Although little is known about aminimide surfactants that contain fluorine, alkyl-substituted acylaminimide surfactants have been reported to possess a low toxicity and have been used in cosmetics [3].

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The hydrophobic properties of polyfluoroalkoxy groups would be expected to be similar to those of polyfluoroalkyl groups and therefore it should be possible to construct potent aminimide surfactants containing a polyfluoroalkoxy group. Such molecules may be particularly useful in forming stable aqueous emulsions of perfluorocarbons. These surfactants would have an oxygen in their hydrophobic chain so that they should be more flexible than surfactant molecules containing rigid perfluoroalkyl groups, and should pack tighter at the fluorocarbon-water interface. For these reasons, we have prepared a variety of amine polyfluoroalkoxyacylimides and examined their surfactant and emulsifying properties.

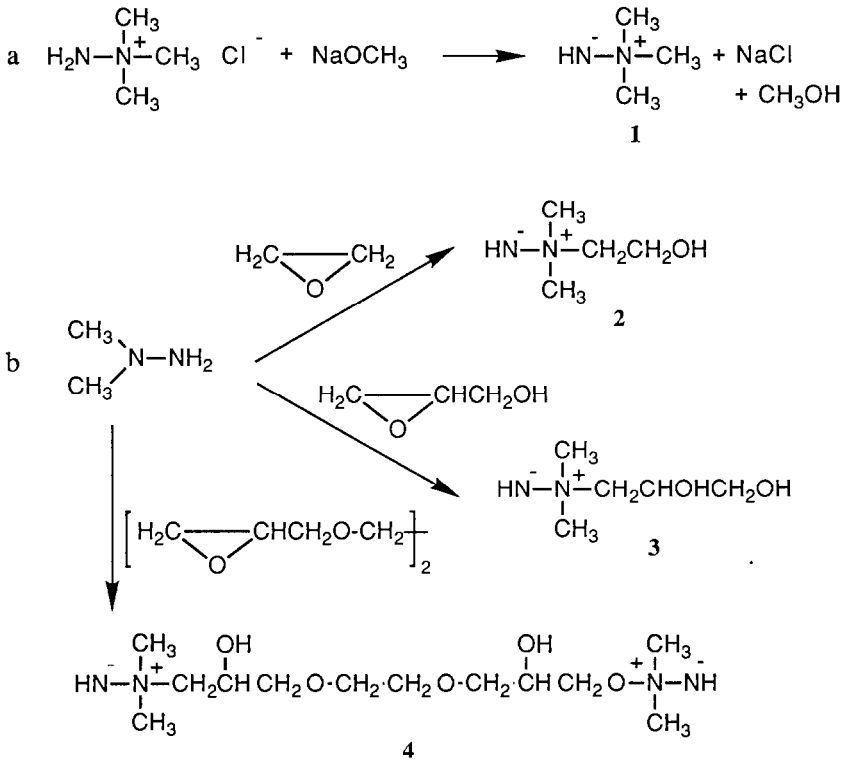
SYNTHESIS

The amine(polyfluoroalkoxyacyl)imides were prepared by the general reaction of a carboxylic acid ester with a tertiary aminimide [3], as illustrated in *Scheme I* (see Tables I, II and III for structures).

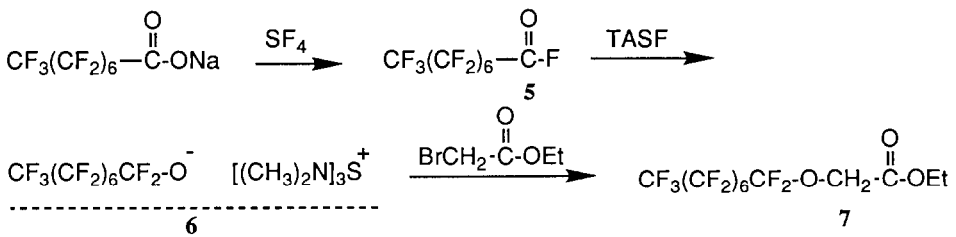
Scheme I

The tertiary aminimides used in these syntheses were all prepared and used *in situ*. Trimethylaminimide (**1**) was generated by the reaction of **1,1,1-trimethylhydrazonium chloride with** sodium methoxide in methanol (*Scheme IIa*). The aminimides containing hydroxy-substituted alkyl groups, (**2**, **3** and **4**), were obtained by the reaction of dimethylhydrazine with the appropriate ethylene oxide in ether or methanol (*Scheme IIb and IIc*). The aminimides **1** and **2** are known compounds [5, 6], but 2,3-dihydroxypropyldimethylaminimide (**3**), and the difunctional aminimide **4** are new compounds. Because of their instability, these new compounds were not isolated, but were characterized by the preparation of acyl derivatives.

Ethyl perfluorooctyloxyacetate, **7**, used in the preparation of surfactant **10a**, was prepared according to *Scheme III*. First, sodium perfluorooctanoate was converted to the acyl fluoride **5** [7] by reaction with sulfur tetrafluoride; compound **5** was then treated with tris(dimethylamino)-sulfonium difluorotrimethylsilicate (TASF) [8] to give the tris(dimethylamino)sulfonium salt of perfluorooctanol, **6**. This activated alkoxide, which is similar to those previously reported [9], was then reacted with ethyl bromoacetate to produce the ester **7**. The sodium and particularly the potassium salts of perfluorooctyloxyacetic acid (**7a** and **7b**, respectively), prepared by the saponification of **7** with NaOH and KOH, are potent surfactants themselves (see Experimental).



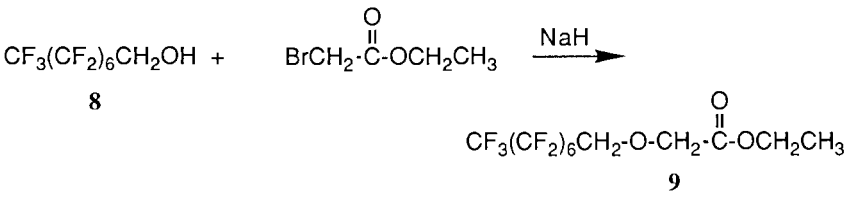
Scheme II



Scheme III

Ethyl 1*H*,1*H*-perfluorooctyloxyacetate, **9**, used in the syntheses of surfactants **11a-d**, was prepared according to *Scheme IV*. First, 1*H*,1*H*-perfluorooctanol (**8**) was prepared by the

reduction of perfluorooctanoyl chloride with sodium bis(2-methoxyethoxy)aluminum hydride and then reacted with sodium hydride and ethyl bromoacetate to give **9**.



Scheme IV

PROPERTIES

The aminacylimide surfactants (**10a-d, 12a**) prepared from the straight-chain esters **7** and **9** showed an outstanding ability to form aqueous solutions with very low surface tensions, with values of 17 dynes/cm or lower. The lowest value obtained was for **10b,** which gave a surface tension of 15.0 dynes/cm for a 0.2% aqueous solution. We believe that these low values are a result of very tight packing of the monolayer formed at the air-liquid interface. This tight packing was confirmed by determining the excess surface concentration (Γ) and surface area occupied by individual molecules at the interface, using the Gibbs equation and surface tension measurements [10]. We obtained values of from 32 to 39 $Å^2$ for the cross-sectional area of aminacylimides prepared from the straight-chain esters **7** and **9**. These values agree very closely to the values calculated from computer generated [11] models of the extended molecules, which indicate a cross-sectional area of about 32 $Å^2$ for these aminacylimides.

A typical graph of surface tension of one of the aminacylimides (**10c**) vs ln concentration, used to calculate the excess surface concentration, is shown in **Fig. 1. The slope of the line** at concentrations below the CMC (critical micelle concentration) is used to calculate Γ [10].

A side view and an end-on view of a computer generated picture of **10c** in a stretched out confirmation **is shown in Fig. 2. The cross sectional area,** 32 $Å^2$, was determined from this picture by assuming the radius of the fluorine atom is 1.35 Å; carbon 1.60 Å; and oxygen 1.35 Å.

The aminacylimides (**11a-l, 12b-e**) prepared from esters derived from hexafluoropropylene (HFPO) oligomers, although still very good surfactants, were not as potent in their ability to form aqueous solutions with very low surface tensions as were the aminacylimides derived from the straight chain esters. This may result from less tight packing at the air-liquid interface, and is consistent with their ' kinky ' structure and larger cross sectional area as indicated by computer

generated models (see Fig. 2). The surfactants prepared from HFPO trimer **11b, 11f, 11j, 12c**) and tetramer (**11c, 11g, 11k, 12d**) appeared to be better than the surfactants prepared from HFPO dimer (**11a, 11e, 11i, 12b**) and pentamer (**11d, 11h, 11l, 12e**). This may be due to a poorer balance between the hydrophilic and hydrophobic properties, with the dimer products being too hydrophilic, and the pentamer products being too hydrophobic. This concept of ' balance ' is in agreement with the observation that **11l** is more potent than **11h**, although they were both prepared from HFPO pentamer. Surfactant **11l** contains a larger hydrophilic group, which helps to balance the large hydrophobic group.

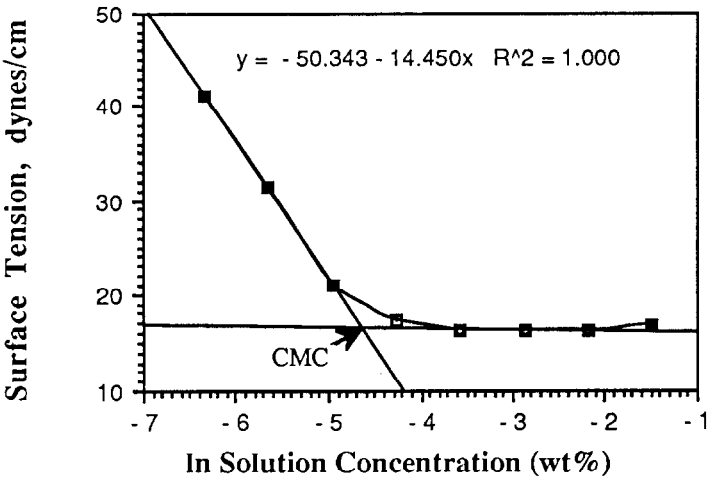


Fig. 1. Surface tension of aqueous solutions of 10c.

None of the aminacylimides derived from HFPO were obtained in crystalline form, but instead were isolated as waxes, glasses, or viscous syrups. This is not surprising, since all of these molecules possess several asymmetric centers and could exist in many isomeric forms. For example, **12e** contains 12 asymmetric carbon atoms, and theoretically could exist in 4064 isomeric forms (32 *meso* and 2016 *dl* pairs).

Emulsions of perfluorodecalin (20 % by weight) in water were prepared by sonication, using the new aminacylimides as emulsifying agents. The ability to form stable emulsions appeared to be directly related to the ability of the aminacylimides to lower the surface tension of water. All of the aminacylimides that gave aqueous solutions with minimum surface tensions of less than 18

dynes/cm also gave emulsions that were stable for at least several months. The aminacylimides that gave surface tension minimums of between 18 and 25 dynes/cm gave emulsions that broke after a few hours to a few weeks, and the aminacylimides that gave higher surface tension minimums gave emulsions that were even less stable.

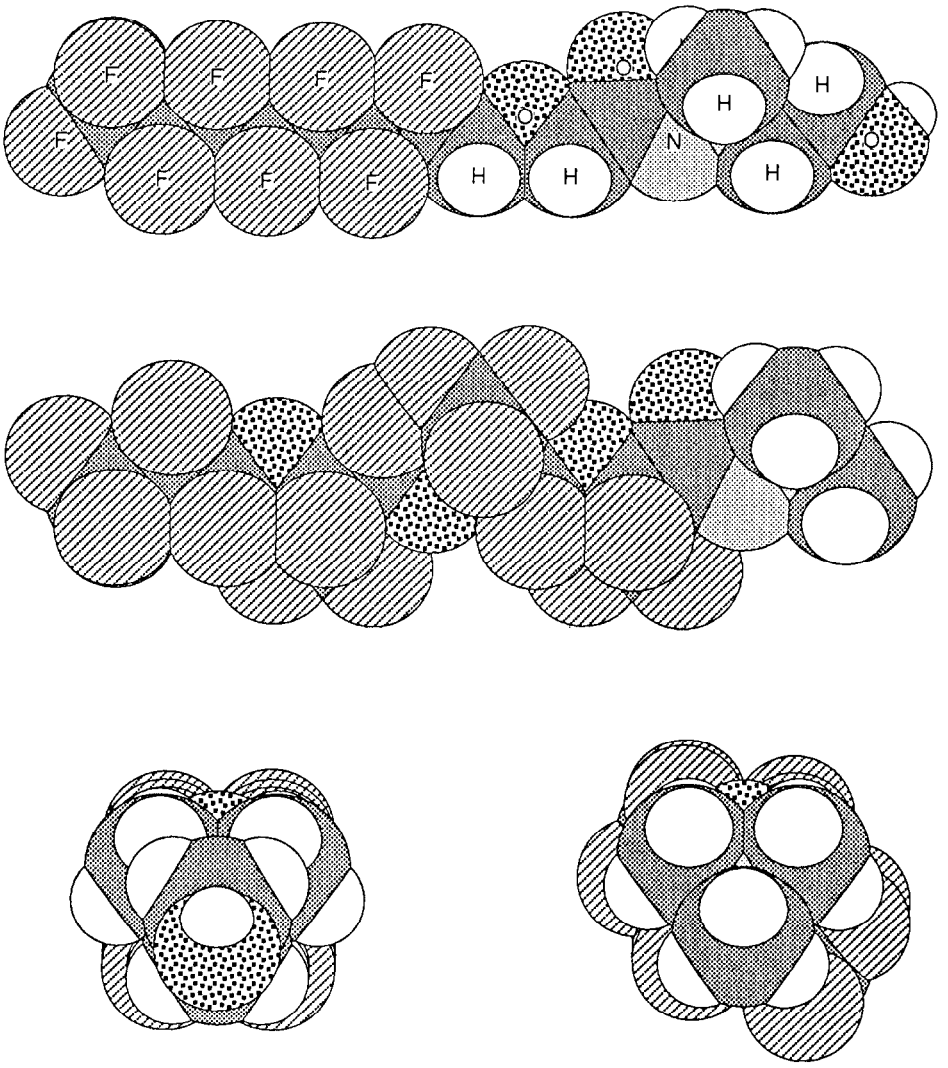
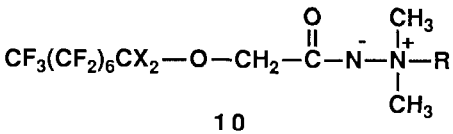


Fig. 2. Side view (top) and end view (bottom left) of a computer generated drawing of **10c** in an extended conformation (not the same scale); side view (middle) and end view (bottom right) of **11b**.

TABLE I

Amine(polyfluorooctyloxyacetyl)imides (10)



10

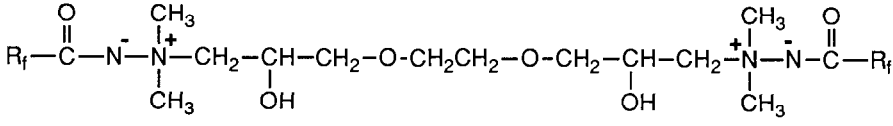
a. X = F, R = -CH_3
b. X = H, R = -CH_3
c. X = H, R = -CH_2CH_2OH
d. X = H, R = -CH_2—CH(OH)—CH_2OH

Cpd. No.	Formula	Yield %	Analysis,% Fluorine Calc.	Fluorine Found	Nitrogen Calc.	Nitrogen Found	IR,cm^{-1} CON	Surface Tension* dynes/cm
10a	$C_{13}H_{11}F_{17}N_2O_2$	70	58.70	58.41	5.09	4.93	1680	16.7
10b	$C_{13}H_{13}F_{15}N_2O_2$	65	55.42	55.40	5.45	5.42	1609	15.
10c	$C_{14}H_{15}F_{15}N_2O_3$	72	52.36	51.99	5.15	4.89	1600	16.2
10d	$C_{15}H_{17}F_{15}N_2O_4$	62	49.62	49.40	4.88	4.72	1593	15.8

* Minimum surface tension for aqueous solutions of ≤ 0.5% concentration.

TABLE II

Diamine-*N*,*N*-bis(acylimides) (12)



12

a. R_f = $-CH_2-O-CH_2(CF_2)_6CF_3$

R_f = $-CF(CF_3)-(O-CF_2-CF(CF_3))_n-F$

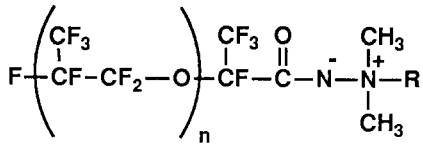
b. n = 1
c. n = 2
d. n = 3
e. n = 4

Cpd. No.	Formula	Yield %	Analysis,% Fluorine Calc.	Fluorine Found	Nitrogen Calc.	Nitrogen Found	IR,cm^{-1} CON	Surface Tension* dynes/cm
12a	$C_{32}H_{36}F_{30}N_4O_8$	99	48.52	48.50	4.77	4.73	1598	16.5
12b	$C_{24}H_{28}F_{22}N_4O_8$	92	45.51	45.40	6.10	5.90	1645-1682	23.5
12c	$C_{30}H_{28}F_{34}N_4O_{10}$	96	51.65	51.28	4.48	4.28	1680	17.1
12d	$C_{36}H_{28}F_{46}N_4O_{12}$	94	55.22	54.92	3.54	3.45	1685	18.2
12e	$C_{42}H_{28}F_{58}N_4O_{14}$	96	57.55	57.15	2.93	2.73	1685	19.0

* Minimum surface tension for aqueous solutions of ≤ 0.5% concentration.

TABLE III

Aminacylimides (11) Derived from Oligomers of Hexafluoropropylene Oxide (11)



11

a. n = 1
b. n = 2
c. n = 3
d. n = 4
} R = -CH_3

e. n = 1
f. n = 2
g. n = 3
h. n = 4
} R = -CH_2CH_2OH

i. n = 1
j. n = 2
k. n = 3
l. n = 4
} R = -CH_2—CH(OH)—CH_2OH

Cpd. No.	Formula	Yield %	Analysis,% Fluorine Calc.	Fluorine Found	Nitrogen Calc.	Nitrogen Found	IR,cm^{-1} CON	Surface Tension dynes/cm
11a	$C_9H_9F_{11}N_2O_2$	56	54.12	53.88	7.25	7.05	1623-1689	32.2
11b	$C_{12}H_9F_{17}N_2O_3$	36	58.49	58.10	5.07	5.05	1627-1685	17.7
11c	$C_{15}H_9F_{23}N_2O_4$	26	60.84	60.45	3.90	3.65	1627-1685	18.3
11d	$C_{18}H_9F_{29}N_2O_5$	82	62.31	62.42	3.17	3.15	1627-1691	24.7
11e	$C_{10}H_{11}F_{11}N_2O_3$	98	50.21	49.99	6.73	6.59	1610-1707	23.4
11f	$C_{13}H_{11}F_{17}N_2O_4$	98	55.47	55.49	4.81	4.59	1631-1691	16.8
11g	$C_{16}H_{11}F_{23}N_2O_5$	94	58.40	58.00	3.74	3.59	1631-1691	21.3
11h	$C_{19}H_{11}F_{29}N_2O_6$	96	60.26	59.97	3.06	2.97	1639-1692	28.7
11i	$C_{11}H_{13}F_{11}N_2O_4$	65	46.83	46.49	6.28	5.99	1610-1684	34.0
11j	$C_{14}H_{13}F_{17}N_2O_5$	53	52.75	52.40	4.58	4.42	1615-1690	17.8
11k	$C_{17}H_{13}F_{23}N_2O_6$	45	56.15	55.89	3.60	3.49	1601-1685	17.6
11l	$C_{20}H_{13}F_{29}N_2O_7$	42	58.35	57.99	2.97	3.00	1610-1685	23.8

* Minimum surface tension for aqueous solutions of ≤ 0.5% concentration.

EXPERIMENTAL

Infrared spectra were recorded on a Perkin-Elmer Model 1310 Infrared spectrophotometer, surface tensions determined by a Fisher Surface Tensiomat ® Model 21, gas chromatographs recorded by a Perkin-Elmer Model 8500 gas chromatograph, and ^{1}H NMR spectra obtained on a Varian EM-360 1H NMR spectrometer using tetramethylsilane as an internal standard. The HFPO oligomer esters were purchased from PCR Incorporated, Gainesville, Florida, U.S.A.

Perfluorooctanoyl Fluoride (5) [7]. Sulfur tetrafluoride, 18 mL (measured at -78°, 0.3 mol) was distilled into a stirred solution of 50.0 g (0.115 mol) of sodium perfluorooctanoate in 100 mL of diglyme at ambient temperature. The mixture was allowed to reflux (cold finger condenser) for 1 hr and then distilled to give 26.3 g (55 %) of **5** as a colorless liquid, bp 108-109°C.

Ethyl Perfluorooctanoxyacetate (7). A 20.01-g (0.048 mol) sample of perfluorooctanoyl fluoride (**5**) was added dropwise to a stirred solution of 13.23 g (0.048 mol) of tris(dimethylamino)sulfonium difluorotrimethylsilicate [8] in 50 mL of acetonitrile at room temperature and under an atmosphere of nitrogen. After the addition, the reaction mixture was evacuated to distill out most of the by-product fluorotrimethylsilane. Ethyl bromoacetate, 8.0 g (0.048 mol), was added dropwise and the reaction mixture was stirred overnight at ambient temperature and then poured into water. The aqueous mixture was extracted with ether and the extracts were washed with water, dried ($MgSO_4$), and distilled to give 7.0 g (28%) of **7** as a colorless liquid: bp 100-102° (2.0 mm); IR (neat) 1710 cm^{-1} (C=O) and 1150-1250 cm^{-1} (CF); ^{1}H NMR (neat) δ 1.37 ppm (t, J = 7 Hz, 2H), δ 4.65 ppm (q, J = 7 Hz, 3H). Anal. Calcd for $C_{12}H_7F_{17}O_3$: F, 61.81. Found: F, 61.50.

Sodium Perfluorooctanoxyacetate (7a). Aqueous sodium hydroxide, 1.68 mL of 1.137 *N* (1.92 mmol), was added dropwise with stirring to a solution of 1.00 g (1.92 mmol) of **7** in 25 mL of ethanol. The reaction mixture was refluxed for 2 hrs, and then evaporated to dryness under reduced pressure to give 0.72 g (73 %) of **7a** as a waxy white solid: mp 225-235°d; IR (nujol) 1690 cm^{-1} (C=O); CMC 0.0097 mole/L; surface tension at CMC, 17.2 dynes/cm. Anal. Calcd for $C_{10}H_2F_{17}O_3Na$: F, 62.58. Found: F, 62.37.

Potassium Perfluorooctanoxyacetate (7b). Aqueous potassium hydroxide, 2.32 mL of 0.8202 *N* (1.92 mmol), was added dropwise with stirring to a solution of 1.00 g (1.92 mmol) of **7** in 25 mL of ethanol. The reaction mixture was refluxed for 2 hrs, and then evaporated to

dryness under reduced pressure to give 0.80 g (78%) of **7b** as a waxy white solid: mp 225-235° d IR (nujol) 1670 cm^{-1} (C=O); CMC 0.022 mole/L; surface tension at CMC, 15.9 dynes/cm. Anal. Calcd for $C_{10}H_2F_{17}O_3K$: F, 60.69. Found: F, 60.30.

Perfluorooctanoyl chloride [7]. A mixture of 82.8 g (0.2 mol) perfluorooctanoic acid, 3 mL *N,N*-dimethylformamide and 59.5 g (0.5 mol) thionyl chloride was refluxed for 4 hours and then distilled to give 78.0 g (90%) of the acid chloride as a colorless liquid: bp 138-141°; IR(neat) 1800 cm^{-1} (C=O).

1*H*,1*H*-Perfluorooctanol (8) [12]. A 51.9-g (0.12 mol) sample of perfluorooctanoyl chloride was added dropwise with stirring to a mixture of 38.8 mL of 3.4 M solution in toluene (0.132 mol) of the reducing agent, Red-Al® (sodium bis(2-methoxyethoxy)aluminum hydride) and 180 mL of anhydrous ether. After the addition, the mixture was refluxed for 30 minutes and then cooled to room temperature. Cold 10 % aqueous hydrochloric acid, 144 mL, was added and the organic layer was separated, washed with water, dried ($MgSO_4$), and distilled to give 36.8 g (77%) of **8** as a colorless liquid, bp 148-150°, that solidifies to a white, waxy solid, mp 46.5°.

1*H*,1*H*-Perfluorooctanoxyacetate (9). A solution of 36.52 g (0.0913 mol) of **8** in 50 mL diglyme was added dropwise to a suspension of 2.4 g (0.1 mol) of sodium hydride in 200 mL of diglyme. When evolution of hydrogen ceased, 15.25 g (0.0913 mol) ethyl bromoacetate was added dropwise with stirring. The mixture was refluxed for 24 hours, cooled and then mixed with 200 mL of methylene chloride, washed several times with water to remove the inorganic salts and diglyme, dried ($MgSO_4$) and distilled to give 18.88 g (43%) of **9** as a clear colorless liquid: bp 82-84° (0.8-0.9 mm); IR (neat) 2998 cm^{-1} (CH), 1760 cm^{-1} (s) (CO); ^1H NMR (neat) δ 1.37 ppm (t, J = 7 Hz, 2H), δ 4.57 ppm (t, J = 28 Hz, 2H), δ 4.59 ppm (q, J = 7 Hz, 3H), δ 4.60 ppm (s, 2H).

1,1,1-Trimethylhydrazonium chloride. Chloromethane, 33 mL (measured at -10°, 0.60 mol) was slowly distilled into a solution of 30.05 g (0.5 mol) 1,1-dimethylhydrazine in 250 mL anhydrous ether. The stirred mixture became immediately cloudy upon the addition of chloromethane and after one hr at room temperature became filled with white crystals. This solid was collected on a filter under an atmosphere of nitrogen to give 33.0 g (50%) of the salt as very hygroscopic white crystals [13].

Trimethylamine(1*H*,1*H*-perfluorooctanoxyacetyl)imide (10b). A 1.26 g (0.114 mol) sample of 1,1,1-trimethylhydrazonium chloride was added to a solution prepared by

dissolving 1.26 g (0.0114 mol) of sodium in 40 mL of methanol, and then 5.50 g (0.113 mol) of ethyl 1*H*,1*H*-perfluorooctanoxyacetate (**9**) was added dropwise with stirring at ambient temperature. The reaction mixture was refluxed overnight and then cooled. The precipitated NaCl was removed by filtration, and the filtrate was evaporated to dryness under reduced pressure. The residue was recrystallized from methanol-ether to give 3.80 g (65.4%) of **10b** as a white, waxy solid, mp 75-77°. In a similar manner, **trimethylamine(perfluorooctanoxy)acetylimide (10a)** was prepared from **7**; **trimethylamine(perfluoro-2-methyl-3-oxahexanoyl)imide (11a)** was prepared from methyl perfluoro-2-methyl-3-oxahexanoate; **trimethylamine(perfluoro-2,5-dimethyl-3,6-dioxanonanoyl)imide (11b)** was prepared from methyl perfluoro-2,5-dimethyl-3,6-dioxanonanoate; **trimethylamine(perfluoro-2,5,8-trimethyl-3,6,9-trioxadodecanoyl)imide (11c)** was prepared from methyl perfluoro-2,5,8-trimethyl-3,6,9-trioxadodecanoate; and **trimethylamine(perfluoro-2,5,8,11-tetramethyl-3,6,9,12-tetraoxapentadecanoyl)imide (11d)** was prepared from methyl perfluoro-2,5,8,11-tetramethyl-3,6,9,12-tetraoxapentadecanoate and purified by titurating with hexane.

2-Hydroxyethyldimethylamine(1*H*,1*H*-perfluorooctanoxyacetyl)imide (10c). Ethylene oxide, 0.815 g (0.0185 mol), was distilled into a flask equipped with a cold-finger condenser and containing a solution of 1.11 g (0.0185 mol) of 1,1-dimethylhydrazine and 5.98 g (0.0123 mol) of **9** in 25 mL of methanol. The reaction mixture was allowed to remain at room-temperature overnight, and then evaporated to dryness under reduced pressure to give 4.83 g (72%) of **10c as** a white semi-solid. In a similar manner, **2-hydroxyethyldimethylamine(perfluoro-2-methyl-3-oxahexanoyl)imide (11e)** was prepared from methyl perfluoro-2-methyl-3-oxahexanoate; **2-hydroxyethyldimethylamine(perfluoro-2,5-dimethyl-3,6-dioxanonanoyl)imide (11f).**was prepared from methyl perfluoro-2,5-dimethyl-3,6-dioxanonanoate; **2-hydroxyethyldimethylamine(perfluoro-2,5,8-trimethyl-3,6,9-trioxadodecanoyl)imide (11g)** was prepared from methyl perfluoro-2,5,8-trimethyl-3,6,9-trioxadodecanoate; and **2-hydroxyethyldimethylamine(perfluoro-2,5,8,11-tetramethyl-3,6,9,12-tetraoxapentadecanoyl)imide (11h)** was prepared from methyl perfluoro-2,5,8,11-tetramethyl-3,6,9,12-tetraoxapentadecanoate.

2,3-Dihydroxypropyldimethylamine-1*H*,1*H*-perfluorooctanoxyacetate (10d). A solution of 1.08 g (0.018 mol) of glycidol in 7 mL of ether was added dropwise to a solution of 1.08 g (0.018 mol) of 1,1-dimethylhydrazine and 5.834 g (0.012 mol) of **9** in 18 mL of ether at room temperature. A mildly exothermic reaction occurred. The reaction mixture was allowed to remain at room temperature overnight. The solvent was decanted from the precipitated

solid, and the solid was washed with several portions of ether and then dried under reduced pressure to give 4.27 g (62 %) of **10d** as a white waxy solid. In a similar manner, **2,3-dihydroxypropyldimethylamine(perfluoro-2-methyl-3-oxahexanoyl)imide (11i)** was prepared from methyl perfluoro-2-methyl-3-oxahexanoate; **2,3-dihydroxypropyldimethylamine(perfluoro-2,5-dimethyl-3,6-dioxanonanoyl)imide (11j)** was prepared from methyl perfluoro-2,5-dimethyl-3,6-dioxanonanoate; **2,3-dihydroxypropyldimethylamine(perfluoro-2,5,8-trimethyl-3,6,9-trioxadodecanoyl)imide (11k)** was prepared from methyl perfluoro-2,5,8-trimethyl-3,6,9-trioxadodecanoate; and **2,3-dihydroxypropyldimethylamine(perfluoro-2,5,8,11-tetramethyl-3,6,9,12-tetraoxapentadecanoyl)imide (11l)** was prepared from methyl perfluoro-2,5,8,11-tetramethyl-3,6,9,12-tetraoxapentadecanoate.

***N,N,N',N'*-Tetramethyl-4,7-dioxa-2,9-dihydroxy-1,10-decanediamine-*N,N'-bis*[(1*H*,1*H*-perfluorooctanoxyacetyl)imide] (12a).** A solution of 0.854 g (0.005 mol) ethylene glycol diglycidol ether in 7 mL of methanol was added dropwise to a stirred solution of 0.89 g (0.015 mol) 1,1-dimethylhydrazine and 4.8 g (0.01 mol) **9** in 23 mL of methanol. The reaction mixture was refluxed overnight and then evaporated to dryness under reduced pressure to give 5.71 g (99 %) of **12a** as a white waxy solid. In a similar manner, ***N,N,N',N'*-tetramethyl-4,7-dioxa-2,9-dihydroxy-1,10-decanediamine-*N,N'-bis*[(perfluoro-2-methyl-3-oxahexanoyl)imide] (12b)** was prepared from methyl perfluoro-2-methyl-3-oxahexanoate, ^{1}H NMR ($CDCl_3$) δ 7.39 ppm (2 OH), δ 3.38 ppm (4 CH_3), 2.58-4.68 ppm (m, 14 other CH); ***N,N,N',N'*-tetramethyl-4,7-dioxa-2,9-dihydroxy-1,10-decanediamine-*N,N'-bis*[(perfluoro-2,5-dimethyl-3,6-dioxanonanoyl)imide] (12c)** was prepared from methyl perfluoro-2,5-dimethyl-3,6-dioxanonanoate; ***N,N,N',N'*-tetramethyl-4,7-dioxa-2,9-dihydroxy-1,10-decanediamine-*N,N'-bis*[(perfluoro-2,5,8-trimethyl-3,6,9-trioxadodecanoyl)imide] (12d)** was prepared from methyl perfluoro-2,5,8-trimethyl-3,6,9-trioxadodecanoate; and ***N,N,N',N'*-tetramethyl-4,7-dioxa-2,9-dihydroxy-1,10-decanediamine-*N,N'-bis*[(perfluoro-2,5,8,11-tetramethyl-3,6,9,12-tetraoxapentadecanoyl)imide] (12e)** was prepared from methyl perfluoro-2,5,8,11-tetramethyl-3,6,9,12-tetraoxapentadecanoate.

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