Symmetric Di- or Tetra-alkyl Substituted Monodisperse Polyoxyethyleneglycols: Synthesis and Surface Properties

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A new series of amphiphilic compounds are presented. The dialkylated monodisperse polyoxyethylene derivatives were prepared by a three-step reaction and global yields >60% were obtained. For the synthesis of the tetraalkylated derivatives, six reaction steps were required and yields >40% were obtained. The evaluation of their surface properties was effected by measuring the variation of the surface tension (γ) of the aqueous solutions as a function of their concentration. The results reveal that they are surface-active agents. They lowered the surface tension of water to the range usually observed for classical hydrogenated non-ionic surfactants. The observed stabilization of γ for a range of concentrations corresponds to the formation of organized phases. The Critical Concentrations obtained are higher than those for analogous linear compounds having the same hydrophilic–lipophilic balance. The areas per polar head group of surfactant molecules are relatively constant for compounds of equivalent hydrophobicity.

Surface-active organic compounds having chelating properties are of current interest and a number of new compounds of this kind have been synthesized in recent years.[1–5] Many of these products mimic the properties of natural ionophores such as monensine[6,7] and have been shown to be good chelants of cations.[8–10] Most of these compounds have an attractive structural feature in that they contain both a hydrophilic moiety (which ensures their chelating properties) and a lipophilic moiety (which generally makes them soluble in an organic medium, thus allowing for the extraction of complexed molecules from an aqueous to an organic phase).

As part of a continuing investigation of the synthesis and physico-chemical properties of amphiphilic substances,[2,3] we have embarked on a project to study the preparation and properties of new monodisperse polyoxyethyleneglycol derivatives (Fig. 1). These molecules have been rendered surface-active by the introduction of symmetrical di- or tetra-alkyl substituted chains. Polyoxyethyleneglycols have been widely used both as cation complexants[11] and as hydrophilic head groups of many surfactant molecules.[12]

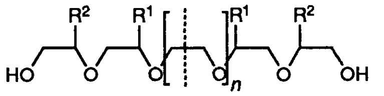


Fig. 1 Structure of the di- or tetra-alkyl polyoxyethyleneglycol derivatives

Results and Discussion

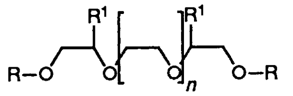
Synthesis.—All the compounds prepared were structurally symmetrical, and their lipophilic character was modified by varying the length of the alkyl groups (C_4 or C_8). The structural symmetry of these compounds appears to favour good surface properties. It can also be predicted that short and identical hydrophobic chains should allow for the formation of organized systems, though with more difficulty than with longer straight-chain alkyl groups. In general, compounds with two hydrophobic chains in the same molecule tend to form either bilayers, vesicles or lamellar phases.[13] It follows then that the observed sharp changes in the physical properties of the aqueous solutions of these substances do not necessarily indicate the formation of micelles.[2] For this reason, the term critical concentration (CC) instead of critical micelle concentration (CMC) is used in this paper to specify the concentration at which a sharp change is observed in the physical properties examined. Therefore, the CC corresponds to the passage of the amphiphilic molecule from a monomeric form to an organized state. *A priori*, the CC values obtained with the compounds prepared are expected to be greater than those obtained with linearly structured surface-active agents with equivalent hydrophobicity. The hydrophilicity of these compounds could be modified by varying the number of the oxyethylene units. The general structure of the compounds prepared is presented in Fig. 1 and the synthetic strategy in Scheme 1. The lipophilic chains were introduced into the molecules by the reaction of the intermediate α-bromocarboxylic acids. The substitution reaction,[14] of these bromo derivatives, was effected by the disodium salts of monodisperse ethyleneglycols.

Introduction of two lipophilic moieties. The reaction of sodium hydride with polyoxyethyleneglycols and the subsequent condensation of α-bromocarboxylic acids (R^1) with the diolates formed, yielded the diacids of oxyethyleneglycol derivatives. However, the difficulties encountered in the purification of these acids were resolved by preparing their methyl ester derivatives. The esters were prepared by reaction of the crude acid products (after treatment and extraction of the product with diethyl ether) with diazomethane. The esters thus formed were easier to purify than the acids by column chromatography. The diesters were obtained in high yields (70–90%).

Reduction of the esters. The esters were reduced to the corresponding glycols (type I) using lithium aluminium hydride in tetrahydrofuran (THF) at 25 °C. Very high yields were obtained (>90%). These glycols can also be used in the preparation of monodisperse tetraalkylated polyoxyethylene glycols.

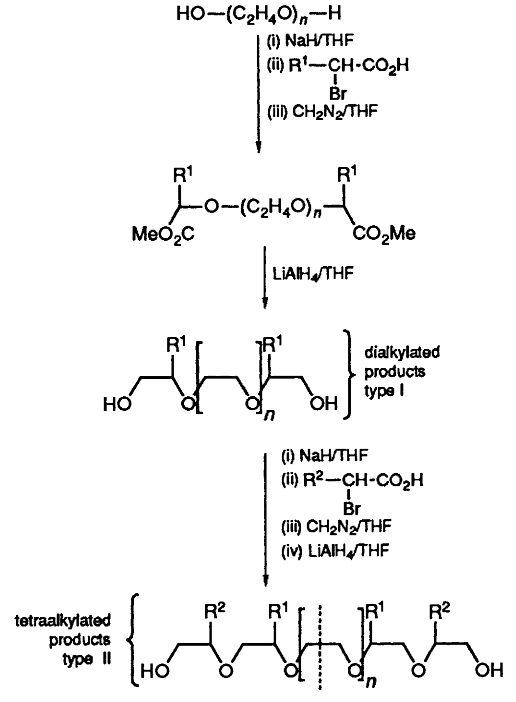
Introduction of four lipophilic moieties. Two additional lipophilic chains (R^2) could be introduced into the dialkylated

Table 1 Preparation of symmetric di- $[C_mC_mE_n]^a$ or tetra-alkylsubstituted $[(C_m)_4E_n]^a$ monodisperse polyoxyethyleneglycols



No.	Code[a]	R	R¹	R²	*n*	Yield[b] (%)	Global[c] yield (%)
1	$C_4C_4E_3$	H	butyl	—	1	97	76
2	$C_4C_4E_4$	HCR^2CH_2OH	H	butyl	0	98	67
3	$C_4C_4E_5$	HCR^2CH_2OH	H	butyl	1	90	63
4	$C_4C_4E_6$	HCR^2CH_2OH	H	butyl	2	92	63
5	$C_8C_8E_3$	H	octyl	—	1	98	76
6	$C_8C_8E_4$	HCR^2CH_2OH	H	octyl	0	98	69
7	$C_8C_8E_5$	HCR^2CH_2OH	H	octyl	1	97	62
8	$C_8C_8E_6$	HCR^2CH_2OH	H	octyl	2	98	71
9	$(C_4)_4E_5$	HCR^2CH_2OH	butyl	butyl	1	96	54
10	$(C_4)_4E_6$	HCR^2CH_2OH	butyl	butyl	2	80	41
11	$(C_8)_4E_5$	HCR^2CH_2OH	octyl	octyl	1	96	46
12	$(C_8)_4E_6$	HCR^2CH_2OH	octyl	octyl	2	98	46

[a] Compounds type I $C_mC_mE_n$ and compounds type II $(C_m)_4E_n$: *m* is the number of methylenes in the tail moiety and *n* the number of ethyleneglycol groups in the hydrophilic part. [b] Yield with regard to 1 mol equivalent of substrate (ester). [c] Yield with regard to an initial 1 mol equivalent of polyoxyethyleneglycol (3 or 6 reaction steps).



Scheme 1 Synthesis of di- or tetra-alkylated surfactants from ethyleneglycols and α-bromocarboxylic acids

glycols to give the tetraalkylated derivatives (type II). The method employed was similar to that described above. In the presence of sodium hydride, condensation of the dialkylated glycol with an α-bromocarboxylic acid, followed by esterification with diazomethane yielded an intermediate diester (70–80%). This was then reduced to the corresponding substituted glycol by lithium aluminium hydride in THF: yields in the range of 80–98% were obtained.

Using this procedure, a series of compounds were prepared in high yields (see Table 1).

Note that the introduction of alkyl chains led to the formation of two asymmetric carbon atoms for type I compounds and four for type II compounds. Therefore, racemic mixtures were obtained. No attempt was made to separate the different stereoisomers. The surface properties of dialkylated glycols, type I, and tetraalkylated glycols, type II, were measured directly with the purified compounds obtained from the reduction steps.

Surface Properties.—The surface tension measurements described in this report were taken with a Dognon-Abribat tensiometer, using the Wilhelmy plate technique.[12] Sets of measurements were taken at 5 min intervals until no significant change occurred. Solutions that contained purified surfactant molecules reached equilibrium values in less than 20 min. When non-purified products were used, a continuous decrease in the surface tension was observed even after 60 min.

The change of γ with the logarithm of the bulk concentration C (mol dm^{-3}) was measured at definite temperatures. This is exemplified by the curves of Figs. 2, 3 and 4, for $C_4C_4E_n$, $C_8C_8E_n$ and $(C_4)_4E_6$ respectively. The surface tension decreased very rapidly until the CC was reached and then remained constant above it.

In addition to the values of CC and γ_{cc} obtained from the plots of γ *vs.* log C, other physical parameters were calculated from these curves. Through the use of the Gibbs adsorption equation,[15] the surface excess at the solution–air interface (Γ) was obtained: $\Gamma = (1/2.3RT) \times (d\gamma/d \log C)$ where Γ is in mol m^{-2}, R is the universal gas constant and T is the absolute temperature. The value of $(d\gamma/d \log C)$ could be directly obtained from the slope of the plot of γ *vs.* log C. In order to calculate the surface excess at the critical concentration, the slope was determined just before the CC. The minimum area occupied by the molecules at the solution–air interface (A_{min}) was calculated from the relation: $A_{min} = (N\Gamma)^{-1}$, where N is Avogadro's number. The results for the surface properties examined are given in Table 2.

The lowering of the surface tension of pure water (*ca.* 72 mN m^{-1} at 25 °C) by the addition of small amounts of the amphiphiles, shows that they are surface-active agents. In most cases, the critical concentrations (CC) were obtained. Where this was not possible owing to the low solubility of type II products, the surface tension of the saturated aqueous solution was measured, *e.g.* aqueous solutions of $(C_4)_4E_5$, $(C_8)_4E_5$, $(C_8)_4E_6$. The surface tension values obtained, as with most hydrogenated amphiphiles, were between 30 and 40 mN m^{-1}.[16]

The CC values for type I compounds are generally higher than those observed with the equivalent linear derivatives, *i.e.* the same number of oxyethylene units (E_n) and an equivalent lipophilic moiety [number of methylene groups (C_n)]. For

Table 2 Surface properties of water–surfactant systems obtained by the surface tension method at 25 °C

No.	Code	CC/10^{-4} mol dm^{-3} [a]	γ_{CC}/mN m^{-1}	dγ/d log C/mN m^{-1} [c]	A_{min}[d]/10^{-2} nm^{2}
2	$C_4C_4E_4$	25.7	36	−15.6	60
3	$C_4C_4E_5$	18.8	35	−14.7	64
4	$C_4C_4E_6$	19.9	33	−17.3	55
6	$C_8C_8E_4$	0.04	30	−17.1	55
7	$C_8C_8E_5$	0.05	30	−19.8	49
8	$C_8C_8E_6$	0.02	31	−20.1	47
9	$(C_4)_4E_5$	—	33[b]	—	—
10	$(C_4)_4E_6$	0.04	34	−21.5	43
11	$(C_8)_4E_5$	—	35[b]	—	—
12	$(C_8)_4E_6$	—	32[b]	—	—

[a] Critical concentration (CC) established by linear regression over experimental points. [b] γ obtained in a saturated aqueous solution of the surfactant ($\gamma_{saturation}$/mN m^{-1}). [c] Slope established by linear regression over experimental points before CC. [d] A_{min}: Area per polar head group of a surfactant molecule adsorbed at the air–water interface obtained from the classical Gibbs equation (see text).

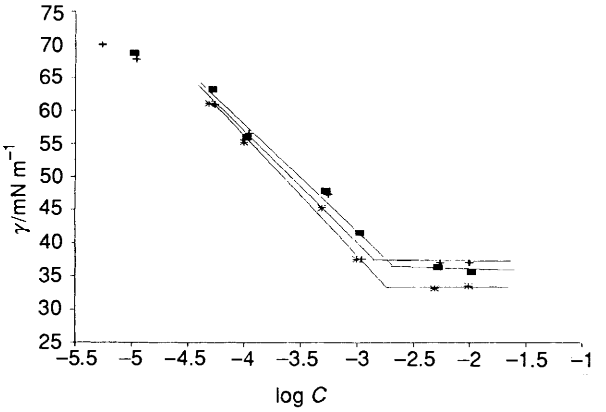


Fig. 2 Surface tension (γ) *versus* log C curves for aqueous solutions of the binary systems water–$C_4C_4E_n$ at 25 °C [n = 4 (■), 5 (+) or 6 (✱)]

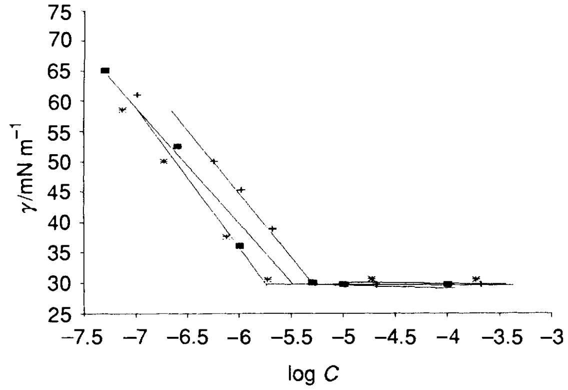


Fig. 3 Surface tension (γ) *versus* log C curves for aqueous solutions of the binary systems water–$C_8C_8E_n$ at 25 °C [n = 4 (■), 5 (+) or 6 (✱)]

example, the CC values of the compounds C_8E_4 (0.85×10^{-4} mol dm^{-3}), C_8E_5 (0.92×10^{-4} mol dm^{-3}) and C_8E_6 (0.99×10^{-4} mol dm^{-3})[16] are lower than those of the equivalent dialkylated products: $C_4C_4E_4$ (25.7×10^{-4} mol dm^{-3}), $C_4C_4E_5$ (19.0×10^{-4} mol dm^{-3}) and $C_4C_4E_6$ (20×10^{-4} mol dm^{-3}) respectively. This observation is also true for the dialkylated derivatives with longer alkyl chains, *i.e.* 2 × C_8. However, only a few of them were sufficiently water soluble to allow the determination of their surface tension at room temperature. Thus, the linear compound $C_{16}E_6$ has a CC value of 1.0×10^{-6} mol dm^{-3}(17) while it was 2.0×10^{-6} mol dm^{-3} for that of $C_8C_8E_6$. It should be noted that the magnitude of the CC depends on the length of the alkyl chain, *e.g.* CC *ca.* 10^{-4} mol dm^{-3} for C_8 and C_4C_4 and *ca.* 10^{-6} mol dm^{-3} for C_{16} and C_8C_8.

The results in Table 2 show that the CCs of these compounds

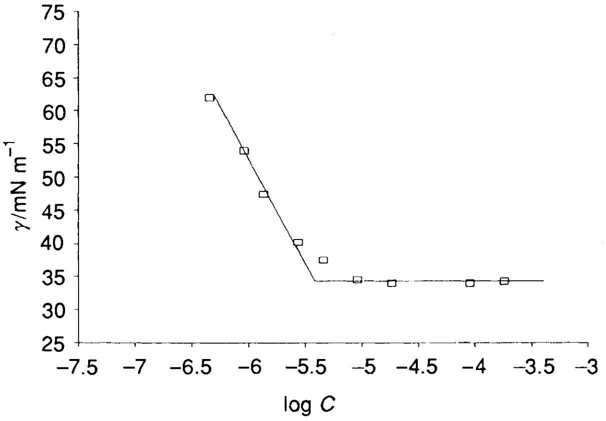


Fig. 4 Surface tension (γ) *versus* log C curves for aqueous solutions of the binary system water–$C_4C_4E_6$ at 25 °C

are not significantly changed by increasing the hydrophilicity of the molecules. Similar results have been reported by Kawashima *et al.*[18] and Rosen *et al.*,[19] using analogous linear amphiphilic compounds. In contrast, the CCs were significantly affected by changing the hydrophobicity of the surfactants. For example, the passage from C_4C_4 to C_8C_8 led to a decrease in CC by a factor of *ca.* 500. For the equivalent linear molecules, a factor of *ca.* 1000 has been reported in the study of the compounds C_9E_8 (CC = 3.0×10^{-3} mol dm^{-3}) and $C_{15}E_8$ (CC = 3.5×10^{-6} mol dm^{-3}).[20]

For type II compounds with four lipophilic moieties $(C_4)_4E_6$, the same CC values of the equivalent lipophilic ($C_8C_8E_n$) was observed. However this value was also lowered by a factor of *ca.* 500 compared to CC values of C_4C_4 compounds. The other tetraalkyl derivatives were only sparingly water soluble, which implies that they could not be used in this comparison. However, the surface tension of their saturated aqueous solutions was measured. The saturated solutions were prepared by shaking the amphiphilic compound in water for *ca.* 10 min at the appropriate temperature. The system was allowed to settle and the appropriate volume of the solution was used for surface tension ($\gamma_{saturation}$) measurement. These sparingly water soluble products can possibly be used to stabilize oil-in-water (or water-in-oil) emulsions or to prepare organized media. Such a use does not require water soluble amphiphiles, although they are generally preferable.

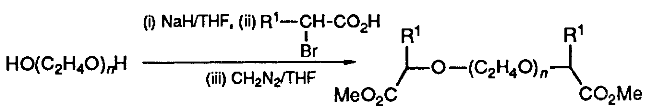
The values of the areas per polar head (A_{min}) deduced from the Gibbs adsorption equation[15] were relatively constant for the compounds $C_4C_4E_n$ ($A_{min} = 60 \pm 6$ Å^2) and $C_8C_8E_n$ ($A_{min} = 50 \pm 6$ Å^2).

A similar observation with phosphoramides was recently reported.[21] As with linear compounds,[2,20] the A_{min} value decreased with an increase in the hydrophobicity of the substituted alkyl oxyethylene derivatives. Comparison of the A_{min} value obtained with the A_{min} values of other amphiphiles within double lipophilic chains (*ca.* 45 Å^2)[13] shows that they are higher in the present compounds. This may be due to the formation of spherical micelles,[13,22] which is indeed unusual for this type of compound. Furthermore, it is even more surprising to observe that the tetraalkyl substituted compound $(C_4)_4E_6$ (A_{min} = 43 Å^2), which has an equivalent hydrophobicity (16 methylenes) to $C_8C_8E_n$, has a lower A_{min} value. This could be attributed to the formation of lamellar or vesicular structures in their aqueous solutions. Nevertheless, the A_{min} data alone cannot be used to draw precise conclusions as to the exact structure of the organized phases. Complementary studies on the phase behaviour (binary and ternary systems), surface and ionophoric properties are now in progress.

Experimental

Preparation of Dialkyl Substituted Glycols (*Type I Compounds*)

Condensation of Ethyleneglycols with α-Bromo Carboxylic Acids and Esterification.—Condensation reactions were carried out under a nitrogen atmosphere and in rigorously anhydrous conditions. 7.7 g of 50% sodium hydride in mineral oil (Fluka) was washed repeatedly with dried THF (20 cm^3) under nitrogen. The suspension of NaH in anhydrous THF (20 cm^3) and ethylene glycol (0.04 mol), corresponding to the desired surfactant structure, were placed in a three-necked flask fitted with a reflux condenser, a thermometer, an addition funnel and magnetic stirrer. After 30 min of constant stirring of this solution at room temperature, two equivalents (0.08 mol) of α-bromo-hexanoic ($R^1 = C_4$) or -decanoic ($R^1 = C_8$) acid in anhydrous THF (20 cm^3) were added. When the addition was complete, the mixture was heated to 65 °C and stirred for 24 h. Water (80 cm^3) was then added. The mixture was concentrated under vacuum. The aqueous phase was acidified with aqueous HCl (2 mol dm^{-3}) and the product was extracted with diethyl ether (3 × 100 cm^3). The combined organic phases were dried ($MgSO_4$) and concentrated under vacuum. The residue was treated with diazomethane (prepared by the *N*-nitrosomethylurea method[23]). The organic mixture was concentrated under vacuum and the crude ester was purified by silica gel column chromatography using light petroleum (40–60 °C) as the eluent (yield of the two steps = 65–80%).



Dimethyl 2,7-*dibutyl*-3,6-*dioxaoctanedioate* (R^1 = butyl, n = 1). Yield 9.9 g (78%), oil; $\delta_H(CDCl_3)$ 4–3.5 [m, 12 H, $(CH_2)_2O$ and OCH_3], 1.85–1.25 (m, 12 H, CH_2 of alkyl chains), 0.9 (t, *J* 6.3 Hz, 6 H, CH_3); ν_{max}(neat)/cm^{-1} 1750 (C=O).

Dimethyl 2,10-*dibutyl*-3,6,9-*trioxaundecanedioate* (R^1 = butyl, n = 2). Yield 9.9 g (68%), oil; $\delta_H(CDCl_3)$ 4.1–3.8 [m, 16 H, $(CH_2)_2O$ and OCH_3], 2.3–1.2 (m, 12 H, CH_2 of alkyl chains), 0.95 (t, *J* 6.3 Hz, 6 H, CH_3); ν_{max}(neat)/cm^{-1} 1745 (C=O).

Dimethyl 2,13-*dibutyl*-3,6,9,12-*tetraoxatetradecanedioate* (R^1 = butyl, n = 3). Yield 11.4 g (70%), oil; $\delta_H(CDCl_3)$ 4–3.45 [m, 20 H, $(CH_2)_2O$ and OCH_3], 2.0–1.15 (m, 12 H, CH_2 of alkyl chains), 0.9 (t, *J* 6.3 Hz, 6 H, CH_3); ν_{max}(neat)/cm^{-1} 1745 (C=O).

Dimethyl 2,16-*dibutyl*-3,6,9,12,15-*pentaoxaheptadecanedioate* (R^1 = butyl, n = 4). Yield 11.9 g (66%), oil; $\delta_H(CDCl_3)$ 3.95–3.5 [m, 24 H, $(CH_2)_2O$ and OCH_3], 1.95–1.15 (m, 12 H, CH_2 of alkyl chains), 0.9 (t, *J* 6.3 Hz, 6 H, CH_3); ν_{max}(neat)/cm^{-1} 1745 (C=O).

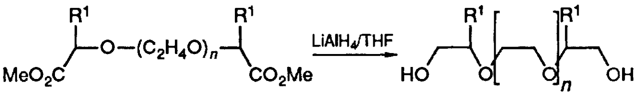
Dimethyl 2,7-*dioctyl*-3,6-*dioxaoctanedioate* (R^1 = octyl, n = 1). Yield 13.4 g (78%), oil; $\delta_H(CDCl_3)$ 4–3.5 [m, 12 H, $(CH_2)_2O$ and OCH_3], 1.8–1.2 (m, 28 H, CH_2 of alkyl chains), 0.9 (t, *J* 6.3 Hz, 6 H, CH_3); ν_{max}(neat)/cm^{-1} 1750 (C=O).

Dimethyl 2,7-*dioctyl*-3,6,9-*trioxaundecanedioate* (R^1 = octyl, n = 2). Yield 13.3 g (70%), oil; $\delta_H(CDCl_3)$ 4.1–3.7 [m, 16 H, $(CH_2)_2O$ and OCH_3], 2.2–1.2 (m, 28 H, CH_2 of alkyl chains), 0.9 (t, *J* 6.3 Hz, 6 H, CH_3); ν_{max}(neat)/cm^{-1} 1745 (C=O).

Dimethyl 2,7-*dioctyl*-3,6,9,12-*tetraoxatetradecanedioate* (R^1 = octyl, n = 3). Yield 13.5 g (65%), oil; $\delta_H(CDCl_3)$ 3.95–3.5 [m, 20 H, $(CH_2)_2O$ and OCH_3], 1.8–1.1 (m, 28 H, CH_2 of alkyl chains), 0.85 (t, *J* 6.3 Hz, 6 H, CH_3); ν_{max}(neat)/cm^{-1} 1745 (C=O).

Dimethyl 2,7-*dioctyl*-3,6,9,12,15-*pentaoxaheptadecanedioate* (R^1 = octyl, n = 4). Yield 17.3 g (77%), oil; $\delta_H(CDCl_3)$ 3.9–3.4 [m, 24 H, $(CH_2)_2O$ and OCH_3], 1.85–1.05 (m, 28 H, CH_2 of alkyl chains), 0.85 (t, *J* 6.3 Hz, 6 H, CH_3); ν_{max}(neat)/cm^{-1} 1750 (C=O).

Reduction of Diesters.—To a solution of 0.02 mol of diester ($R^1 = C_4$ or C_8) in anhydrous THF (150 cm^3) under a nitrogen atmosphere were added, in small portions, two equivalents (0.04 mol) of lithium aluminium hydride at room temperature. After addition the solution was vigorously stirred for 3 h. After hydrolysis (100 cm^3 of water), filtration and extraction of the precipitate with THF, the organic phase was concentrated under vacuum and pure glycols obtained.



2,7-*Dibutyl*-3,6-*dioxaoctane*-1,8-*diol* ($C_4C_4E_3$) **1**. Yield 5.1 g (97%), oil; $\delta_H(CDCl_3)$ 3.80–3.40 [m, 10 H, $(CH_2)_2O$], 1.60–1.20 (m, 12 H, CH_2 of alkyl chains), 0.9 (t, *J* 6.3 Hz, 6 H, CH_3); ν_{max}(neat)/cm^{-1} 3600–3100 (OH).

2,10-*Dibutyl*-3,6,9-*trioxaundecane*-1,11-*diol* ($C_4C_4E_4$) **2**. Yield 6 g (98%), oil; $\delta_H(CDCl_3)$ 3.8–3.1 [m, 14 H, $(CH_2)_2O$], 1.50–1.15 (m, 12 H, CH_2 of alkyl chains), 0.9 (t, *J* 6.3 Hz, 6 H, CH_3); ν_{max}(neat)/cm^{-1} 3600–3100 (OH).

2,13-*Dibutyl*-3,6,9,12-*tetraoxatetradecane*-1,14-*diol* ($C_4C_4E_5$) **3**. Yield 6.3 g (90%), oil; $\delta_H(CDCl_3)$ 3.8–3.4 [m, 18 H, $(CH_2)_2O$], 1.6–1.20 (m, 12 H, CH_2 of alkyl chains), 0.9 (t, *J* 6.3 Hz, 6 H, CH_3); ν_{max}(neat)/cm^{-1} 3600–3100 (OH).

2,16-*Dibutyl*-3,6,9,12,15-*pentaoxaheptadecane*-1,17-*diol* ($C_4C_4E_6$) **4**. Yield 7.3 g (92%), oil; $\delta_H(CDCl_3)$ 3.7–3.15 [m, 22 H, $(CH_2)_2O$], 1.50–1.2 (m, 12 H, CH_2 of alkyl chains), 0.9 (t, *J* 6.3 Hz, 6 H, CH_3); ν_{max}(neat)/cm^{-1} 3600–3100 (OH).

2,7-*Dioctyl*-3,6-*dioxaoctane*-1,8-*diol* ($C_8C_8E_3$) **5**. Yield 7.3 g (98%), oil; $\delta_H(CDCl_3)$ 3.8–3.3 [m, 10 H, $(CH_2)_2O$], 1.6–1.1 (m, 28 H, CH_2 of alkyl chains), 0.9 (t, *J* 6.3 Hz, 6 H, CH_3); ν_{max}(neat)/cm^{-1} 3600–3100 (OH).

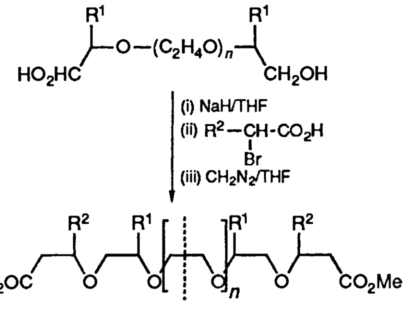
2,10-*Dioctyl*-3,6,9-*trioxaundecane*-1,11-*diol* ($C_8C_8E_4$) **6**. Yield 8.2 g (98%), oil; $\delta_H(CDCl_3)$ 3.8–3.2 [m, 14 H, $(CH_2)_2O$], 1.55–1.15 (m, 28 H, CH_2 of alkyl chains), 0.9 (t, *J* 6.3 Hz, 6 H, CH_3); ν_{max}(neat)/cm^{-1} 3600–3100 (OH).

2,13-*Dioctyl*-3,6,9,12-*tetraoxatetradecane*-1,14-*diol* ($C_8C_8E_5$) **7**. Yield 9 g (97%), oil; $\delta_H(CDCl_3)$ 3.8–3.35 [m, 18 H, $(CH_2)_2O$], 1.65–1.2 (m, 28 H, CH_2 of alkyl chains), 0.95 (t, *J* 6.3 Hz, 6 H, CH_3); ν_{max}(neat)/cm^{-1} 3600–3100 (OH).

2,16-*Dioctyl*-3,6,9,12,15-*pentaoxaheptadecane*-1,17-*diol* ($C_8C_8E_6$) **8**. Yield 9.9 g (98%), oil; $\delta_H(CDCl_3)$ 3.75–3.1 [m, 22 H, $(CH_2)_2O$], 1.6–1.2 (m, 28 H, CH_2 of alkyl chains), 0.9 (t, *J* 6.3 Hz, 6 H, CH_3); ν_{max}(neat)/cm^{-1} 3600–3100 (OH).

Preparation of Tetraalkyl Substituted Glycols (Type II Compounds)

Condensation of Disubstituted Ethyleneglycols with α-Bromo Carboxylic Acids and subsequent Esterification.—The condensation and esterification were realized with identical procedures to those used in the preparation of the disubstituted esters described above.



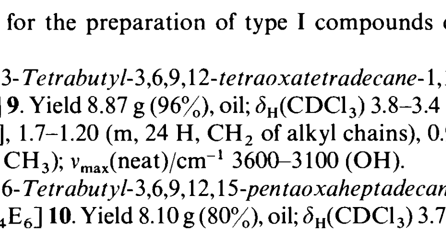
Dimethyl 2,5,10,13-*tetrabutyl*-3,6,9,12-*tetraoxatetradecanedioate* ($R^1 = R^2$ = butyl, $n = 1$). Yield 15.33 g (74%), oil; $\delta_H(CDCl_3)$ 3.90–3.20 [m, 18 H, $(CH_2)_2O$ and OCH_3], 1.80–1.20 (m, 24 H, CH_2 of alkyl chains), 0.90 (t, J 6.3 Hz, 12 H, CH_3); ν_{max}(neat)/cm^{-1} 1750 (C=O).

Dimethyl 2,5,13,16-*tetrabutyl*-3,6,9,12,15-*pentaoxaheptadecanedioate* ($R^1 = R^2$ = butyl, $n = 2$). Yield 13.50 g (60%), oil; $\delta_H(CDCl_3)$3.90–3.20 [m, 22 H, $(CH_2)_2O$ and OCH_3], 1.85–1.25 (m, 24 H, CH_2 of alkyl chains), 0.90 (t, J 6.3 Hz, 12 H, CH_3); ν_{max}(neat)/cm^{-1} 1745 (C=O).

Dimethyl 2,5,10,13-*tetraoctyl*-3,6,9,12-*tetraoxatetradecanedioate* ($R^1 = R^2$ = octyl, $n = 1$). Yield 15.27 g (63%), oil; $\delta_H(CDCl_3)$ 3.90–3.20 [m, 18 H, $(CH_2)_2O$ and OCH_3], 1.80–1.20 (m, 56 H, CH_2 of alkyl chains), 0.90 (t, J 6.3 Hz, 12 H, CH_3); ν_{max}(neat)/cm^{-1} 1750 (C=O).

Dimethyl 2,5,13,16-*tetraoctyl*-3,6,9,12,15-*pentaoxaheptadecanedioate* ($R^1 = R^2$ = octyl, $n = 2$). Yield 17.20 g, (66%), oil; $\delta_H(CDCl_3)$3.90–3.20 [m, 22 H, $(CH_2)_2O$ and OCH_3], 1.85–1.25 (m, 56 H, CH_2 of alkyl chains), 0.90 (t, J 6.3 Hz, 12 H, CH_3); ν_{max}(neat)/cm^{-1} 1745 (C=O).

Reduction of the Diesters.—The procedure was identical to that used for the preparation of type I compounds described above.



2,5,10,13-*Tetrabutyl*-3,6,9,12-*tetraoxatetradecane*-1,14-*diol* $[(C_4)_4E_5]$ **9**. Yield 8.87 g (96%), oil; $\delta_H(CDCl_3)$ 3.8–3.4 [m, 16 H, $(CH_2)_2O$], 1.7–1.20 (m, 24 H, CH_2 of alkyl chains), 0.9 (t, J 6.3 Hz, 12 H, CH_3); ν_{max}(neat)/cm^{-1} 3600–3100 (OH).

2,5,13,16-*Tetrabutyl*-3,6,9,12,15-*pentaoxaheptadecane*-1,17-*diol* $[(C_4)_4E_6]$ **10**. Yield 8.10 g (80%), oil; $\delta_H(CDCl_3)$ 3.75–3.2 [m, 20 H, $(CH_2)_2O$], 2–1.2 (m, 24 H, CH_2 of alkyl chains), 0.9 (t, J 6.3 Hz, 12 H, CH_3); ν_{max}(neat)/cm^{-1} 3600–3100 (OH).

2,5,10,13-*Tetraoctyl*-3,6,9,12-*tetraoxatetradecane*-1,14-*diol* $[(C_8)_4E_5]$ **11**. Yield 10.56 g (96%), oil; $\delta_H(CDCl_3)$ 3.8–3.2 [m, 16 H, $(CH_2)_2O$], 1.6–1.20 (m, 56 H, CH_2 of alkyl chains), 0.9 (t, J 6.3 Hz, 12 H, CH_3); ν_{max}(neat)/cm^{-1} 3600–3100 (OH).

2,5,13,16-*Tetraoctyl*-3,6,9,12,15-*pentaoxaheptadecane*-1,17-*diol* $[(C_8)_4E_6]$ **12**. Yield 11.64 g (98%), oil; $\delta_H(CDCl_3)$ 3.8–3.2 [m, 20 H, $(CH_2)_2O$], 2–1.2 (m, 56 H, CH_2 of alkyl chains), 0.9 (t, J 6.3 Hz, 12 H, CH_3); ν_{max}(neat)/cm^{-1} 3600–3100 (OH).

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