was further stirred at 12 °C for 15 min. The reaction mixture was poured into ice-cold water containing $NaHCO_3$ and extracted with EtOAc (2 × 75 mL). The combined organic extracts were washed with saturated $NaHCO_3$ solution and brine to neutrality. The solvent was dried and removed under oil pump vacuum at −15 °C. The residue was chromatographed on silica gel at 0 °C with *n*-hexane (75 mL), $CH_2Cl_2$–*n*-hexane (1:9, 175 mL), and $CH_2Cl_2$ (250 mL), which gave a bromohydrin **33** (75 mg, 41%), mp 133–135 °C: $^1H$ NMR δ 2.1–2.2 (m, 1 $H_2$), 2.35–2.47 (m, 1 $H_2$), 2.65 (d, 1 $H_{OH}$), 3.03 (s, 3 $H_{7\text{-}Me}$), 3.12 (s, 3 $H_{12\text{-}Me}$), 3.4–3.6 (m, 2 $H_1$), 4.53 (m, 1 $H_3$), 5.10 (t, $J_{app}$ = 5.4, 1 $H_4$), 7.51–7.54 (m, 3 $H_{5,9,10}$), 8.17 (d, 1 $H_6$), 8.25–8.30 (m, 2 $H_{8,11}$), $J_{4,OH}$ = 5.1, $J_{5,6}$ = 9.2; mass spectrum, *m/z* (relative intensity) 356 (14), 354 (13), 338 (26), 336 (26), 323 (10), 321 (10), 275 (8), 274 (22), 260 (13), 258 (15), 256 (69); exact mass calcd for $C_{20}H_{19}OBr$ 356.0594 and 354.0614, obsd 356.0587 and 354.0611. Chromatography also gave bromoacetate **34** (4.2 mg, 2%), mp 81–84 °C: $^1H$ NMR δ 2.1–2.35 (m, 2 $H_2$), 2.17 (s, 3 $H_{4\text{-}Ac}$), 3.03 (s, 3 $H_{7\text{-}Me}$), 3.17 (s, 3 $H_{12\text{-}Me}$), 3.45 (m, 1 $H_1$), 3.56–3.74 (m, 1 $H_1$), 4.52–4.60 (m, 1 $H_3$), 6.40 (d, 1 $H_4$), 7.17 (d, 1 $H_5$), 7.46–7.56 (m, 2 $H_{9,10}$), 8.14 (d, 1 $H_6$), 8.22–8.33 (m, 2 $H_{8,11}$), $J_{3,4}$ = 4.7, $J_{5,6}$ = 9.2; mass spectrum, *m/z* (relative intensity) 398 (13), 396 (17), 316 (23), 275 (17), 274 (58), 260 (11), 259 (33), 258 (69), 257 (100), 256 (25), 242 (91); exact mass calcd for $C_{22}H_{21}O_2Br$ 398.0699 and 396.0719, obsd 398.0704 and 396.0725.

**3,4-Epoxy-7-methyl-1,2,3,4-tetrahydrobenz[*a*]anthracene (35).** A mixture of bromohydrin **31** (25 mg), Amberlite IRA 400 (−OH) (6.5 g), and dry THF (8 mL) was stirred at room temperature, under Ar, with protection from light, for 45 min. The mixture was filtered, and the resin was washed with dry $CH_2Cl_2$. The organic phases were combined, and evaporated, leaving 19 mg (99%) of epoxide **35**, mp 134–135 °C: $^1H$ NMR δ 1.87–1.99 (dt, 1 H), 2.65–2.73 (dd, 1 H), 2.84–2.98 (m, 1 H), 3.56–3.64 (dd, 1 H), 3.89 (br s, $H_3$), 4.03 (d, $H_4$), 7.43–7.57 (m, 3 $H_{5,9,10}$), 8.02 (d, $H_{11}$), 8.22 (d, $H_{6,8}$, *J* = 8.9); 8.28 (d, $H_{6,8}$, *J* = 8.6), 8.54 (s, $H_{12}$), $J_{3,4}$ = 4.2, $J_{10,11}$ = 7.8; mass spectrum (12 eV), *m/z* (relative intensity) 260 (100), 245 (11); exact mass calcd for $C_{19}H_{16}O$ 260.1201, found 260.1199.

**3,4-Epoxy-12-methyl-1,2,3,4-tetrahydrobenz[*a*]anthracene (36).** Bromohydrin **32** (70 mg) in dry THF (8 mL) was added to Amberlite IRA 400 (−OH) (15 g), which had been extensively washed with dry THF, and then covered with 2 mL of dry THF. The mixture was stirred, under Ar, protected from light, for 50 min. The mixture was filtered, and the resin was washed with dry $CH_2Cl_2$. The organic solvents were combined and evaporated at 0 °C to give 53 mg (100%) of epoxide **36**, mp 115–116 °C: $^1H$ NMR δ 1.47–1.59 (m, 1 H), 2.50–2.58 (m, 1 H), 3.35–3.43 (m, 2 H), 3.81 (br s, 1 $H_3$), 4.04 (d, 1 $H_4$), 7.40 (d, 1 $H_5$), 7.43–7.55 (m, 2 $H_{9,10}$), 7.81 (d, 1 $H_{6,8}$, *J* = 8.5), 7.96 (d, 1 $H_{6,8}$, *J* = 8.4), 8.23 (d, 1 $H_{11}$), 8.25 (s, 1 $H_7$), $J_{3,4}$ = 4.2, $J_{5,6}$ = 8.5, $J_{10,11}$ = 8.4; mass spectrum (12 eV), *m/z* (relative intensity) 260 (66), 245 (11); exact mass calcd for $C_{19}H_{16}O$ 260.1201, found 260.1212.

**7,12-Dimethyl-3,4-epoxy-1,2,3,4-tetrahydrobenz[*a*]anthracene (37).** Into a dry 100-mL round-bottomed flask, containing a magnetic stir bar, was placed Amberlite IRA-400 ($^-$OH) (20 g). The flask was evacuated five times and then filled with $N_2$ each time. To this was added bromohydrin **33** (75.4 mg, 0.21 mmol) in dry THF (10 mL), just covering the resin. The mixture, protected from light, was stirred under $N_2$ atmosphere at room temperature for 2 h and then was filtered under suction. The resin was washed with dry $CH_2Cl_2$ (3 × 15 mL). The filtrate was evaporated at 0 °C under high vacuum to obtain the epoxide **37** (58.1 mg, 99%), mp 137–140 °C: $^1H$ NMR δ 1.45–1.55 (m, 1 $H_2$), 2.45–2.58 (m, 1 $H_2$), 3.06 (s, 3 $H_{7\text{-}Me}$), 3.13 (s, 3 $H_{12\text{-}Me}$), 3.2–3.5 (m, 2 $H_1$), 3.80 (t, 1 $H_3$), 4.06 (d, 1 $H_4$), 7.45 (d, 1 $H_5$), 7.49–7.53 (m, 2 $H_{9,10}$), 8.15 (d, 1 $H_6$), 8.24–8.29 (m, 2 $H_{8,11}$), $J_{3,4}$ = 4.2, $J_{5,6}$ = 8.8; mass spectrum, *m/z* (relative intensity) 274 (100), 259 (28), 258 (6), 246 (26), 245 (17), 231 (36); exact mass calcd for $C_{20}H_{18}O$ 274.1353, found 274.1358.

# Phase-Transfer-Catalyzed Synthesis of Oligoethylene Glycols and Derivatives

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An efficient, two-step synthetic method for the addition of ethyleneoxy units to diols is reported. Reaction of HOROH with $Cl(CH_2CH_2O)_nTHP$ and 50% aqueous NaOH in the presence of a phase-transfer catalyst gives $THP(OCH_2CH_2)_nORO(CH_2CH_2O)_nTHP$ from which the protecting groups are readily removed to provide $H(OCH_2CH_2)_nORO(CH_2CH_2O)_nH$ in good-to-excellent yields. The influence of reactant diol structure upon yield has been determined.

Oligoethylene glycols are important building blocks for the synthesis of crown ethers.[1] Although the lower members of the oligoethylene glycol family have been readily accessible as pure compounds for many years, only recently have $HO(CH_2CH_2O)_nH$ with $n > 5$ become commercially available. Functionalized oligoethylene glycols, which are important for the preparation of functionazlied crown ethers and cryptands,[2-5] must be synthesized.

The preparation of individual oligoethylene glycols has been of interest for more than half a century. Most of the reported procedures employ a classical Williamson ether synthesis and provide yields in the 20–45% range.[6-11] In some cases, pure higher oligoethylene glycols were separated from oligoethylene glycol mixtures by fractional

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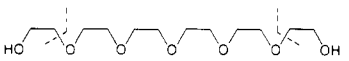
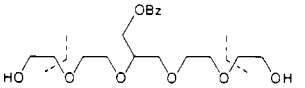
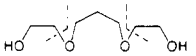
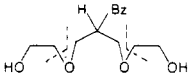
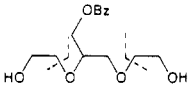
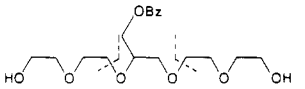
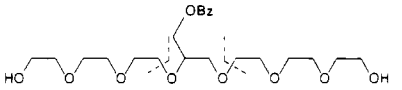
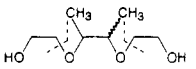
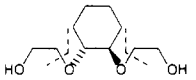
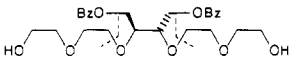
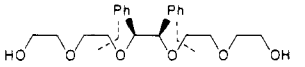
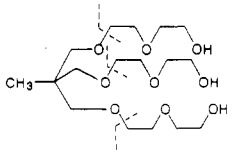
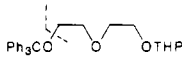
**Table I. Oligoethylene Glycol and Substituted Oligoethylene Glycol Products**

| entry | product[a] | yield,[b] % | ref for previous synthesis |
|---|---|---|---|
| 1 |  | 80 | 6, 11, 15 |
| 2 |  | 87 | 3 |
| 3 |  | 80 | 20, 21 |
| 4 |  | 85 | *c* |
| 5 |  | 75 | 4 |
| 6 |  | 77 | 3 |
| 7 |  | 61 | 4 |
| 8 |  | 78 | 25 |
| 9 |  | 75 | 26 |
| 10 |  | 57 | *c* |
| 11 |  | 46 | *c* |
| 12 |  | 62 | *c* |
| 13 |  | 13 | *c* |

[a] Dashed lines on the structure indicate the diol reactant (center portion) and the ethyleneoxy units, which were added to each side. [b] Overall yields from two steps, except for entry 13. [c] New compound with characterization given in the Experimental Section.

distillation under high vacuum.[12-13] In a recent published procedure, benzyl-protected glycols and monochlorohydrins were utilized in a Williamson ether synthesis followed by debenzylation to produce penta- to nonaethylene glycols in 45–65% yields.[14] In another recent paper, hexaethylene glycol was synthesized by reaction of excess triethylene glycol with tosyl chloride in dioxane followed by addition of powdered sodium hydroxide.[15] Similarly, octaethylene glycol was prepared from tetraethylene glycol.[15]

In 1975, Freedman and Dubois reported an improved Williamson ether synthesis using phase transfer catalysis (PTC).[16] More recently, Nouguier and Mchich have examined alkylation of the hydrophilic polyols pentaerythritol and tris(hydroxymethyl)propane with allyl bromide and heptyl bromide under PTC conditions.[17-19]

We now report the preparation of hexaethylene glycol and structurally modified oligoethylene glycols by an efficient, two-step synthesis in which PTC is employed.

## Results and Discussion

An organic phase of tetraethylene glycol and $ClCH_2CH_2OTHP$ in which an excess of the latter served as the solvent was stirred with 50% aqueous sodium hydroxide in the presence of tetrabutylammonium hydrogen sulfate as the phase-transfer catalyst at 65 °C for 3 days. Following workup of the di-THP-protected hexaethylene glycol product, facile acid-catalyzed deprotection gave hexaethylene glycol in 80% an isolated overall yield (eq 1).

Encouraged by this result, we examined reactions of other diols in which both hydroxyl groups were primary

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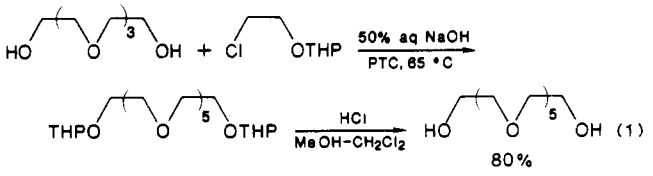


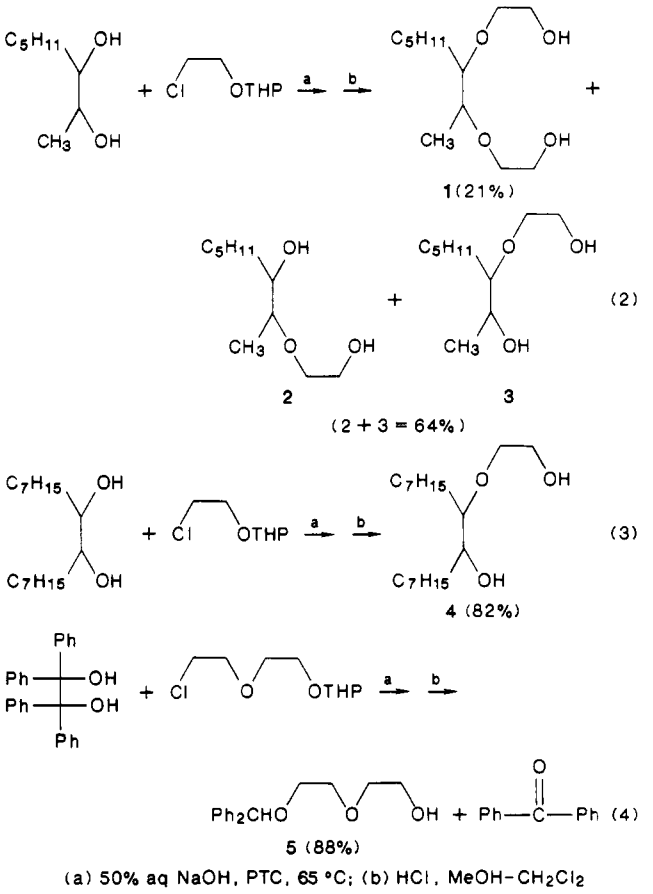

with $ClCH_2CH_2OTHP$ under the same PTC reaction conditions, followed by deprotection (entries 2–4, Table I). In all three cases, high (80–87%) isolated yields of the modified oligoethylene glycols were obtained.

Comparison of this method for the preparation of 1,9-dihydroxy-3,7-dioxanonane (entry 3) with alternative synthetic routes is instructive. The first reported synthesis of this compound was from 1,3-dibromopropane, NaH, and excess ethylene glycol in an unspecified yield.[20] (In our hands, the yield has been 10–15%.) Alternatively, reaction of 1,3-propanediol, chloroacetic acid, and *t*-BuOK in *t*-BuOH followed by reduction of the resultant diacid gave a 32% overall yield of 1,9-dihydroxy-3,7-dioxanonane.[21] From reaction of 1,3-propanediol, NaH, and $ClCH_2CH_2O$-THP in THF, we obtained none of the desired diol. Thus, the 80% overall yield of 1,9-dihydroxy-3,7-dioxanonane achieved by the PTC reaction of 1,3-propanediol with $ClCH_2CH_2OTHP$ followed by deprotection is demonstrated to be markedly superior to those obtained from three alternative synthetic routes.

To explore further the potential of this new procedure for the addition of ethyleneoxy units to diols, reactions of $BzOCH_2CH(OH)CH_2OH$,[22] a functionalized ethylene glycol with one primary and one secondary hydroxyl group, with $ClCH_2CH_2OTHP$ were conducted. A 75% yield of the functionalized triethylene glycol product was obtained (entry 5). Although a 77% yield was obtained when $BzOCH_2CH(OH)CH_2OH$ was reacted with $Cl(CH_2CH_2O)_2THP$ (entry 6), the yield of functionalized oligoethylene glycol was lowered to 61% for reaction with $Cl(CH_2CH_2O)_3THP$ (entry 7). Presumably the lower yield for the latter results from the onset of steric factors.

For (±)-2,3-butanediol and *trans*-1,2-cyclohexanediol, in which both hydroxyl groups are secondary, reactions with $ClCH_2CH_2OTHP$ produced modified triethylene glycols in yields of 78 and 75%, respectively (entries 8 and 9). However, when the starting diol was (±)-2,3-octanediol, a mixture of mono- and disubstituted products was obtained (eq 2). For 8,9-hexadecanediol,[23] an even more hindered and lipophilic diol, reaction with $ClCH_2CH_2OTHP$ and deprotection gave the monoalkylated product in 82% yield, but no dialkylated product was isolated (eq 3).

Reaction of $BzOCH_2CH(OH)CH(OH)CH_2OBz$,[24] which has two secondary hydroxyl groups, with $Cl(CH_2CH_2O)_2OTHP$ followed by deprotection gave a 57% yield of dialkylated product (entry 10). This yield is substantially lower than that achieved for the analogous dialkylation of $BzOCH_2CH(OH)CH_2OH$ (entry 6). Structural modification of the diol component to *meso*-PhCH(OH)CH(OH)Ph (hydroxybenzoin) gave a 46% yield of dialkylated product upon reaction with $Cl(CH_2CH_2O)_2THP$ followed by deprotection (entry 11).




(a) 50% aq NaOH, PTC, 65 °C; (b) HCl, $MeOH-CH_2Cl_2$

One substrate with three primary hydroxyl groups was examined. Reaction of $CH_3C(CH_2OH)_3$ with $Cl(CH_2CH_2O)_2THP$ and subsequent deprotection gave a 62% yield of the trialkylated product (entry 12).

To probe the potential for extension of this PTC reaction to tertiary alcohol centers, reaction of triphenylmethanol with $Cl(CH_2CH_2O)_2THP$ was conducted. A 33% yield of the alkylation product was realized (entry 13). On the other hand, very low yields (<10%) of alkylation products were obtained from three aliphatic tertiary alcohols: 2-methyl-2-propanol, 2-methyl-2-butanol, and 2-methyl-2-undecanol.

From reaction of $Ph_2C(OH)C(OH)Ph_2$ (benzopinacol), which possesses two tertiary hydroxyl groups, with $Cl(CH_2CH_2O)_2THP$ followed by deprotection, an 88% yield of $Ph_2CHO(CH_2CH_2O)_2H$ was isolated, in addition to benzophenone (eq 4). Apparently deprotonation of one hydroxyl group is followed by cleavage to produce a molecule of benzophenone and the alkoxide of diphenylmethanol (benzhydrol), which is subsequently alkylated.

A common feature for all of the PTC alkylations described above is the formation of certain byproducts. As shown by $^1H$ NMR spectroscopy, competitive dehydrochlorination of $Cl(CH_2CH_2O)_nTHP$ takes place to produce $CH_2{=}CHO(CH_2CH_2O)_{n-1}THP$. Also high-boiling dimers $THPO(CH_2CH_2O)_{2n}THP$ apparently arise by reaction of $Cl(CH_2CH_2O)_nTHP$ with hydroxide ion to form $HO(CH_2CH_2O)_nTHP$, which deprotonates and couples with another molecule of $Cl(CH_2CH_2O)_nTHP$. Both of these side reactions take place slower than the desired PTC alkylations and convert some of the excess $Cl(CH_2CH_2O)_nTHP$ into volatile vinyl ethers and high-boiling dimers, which simplifies purification of the alkylation products. Hence, even though the PTC alkylations of primary alcohols are probably complete within a few hours,[16] the additional reaction period was utilized to

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partially consume the excess of alkylating agent.

In summary, we have shown that PTC reactions of diols possessing two primary hydroxyl groups or one primary and one secondary alcohol function with Cl-$(CH_2CH_2O)_n$THP followed by acid-catalyzed deprotection produces oligoethylene glycol derivatives in good-to-excellent yields, which are generally higher than those from alternative synthetic routes. For diols that contain two secondary hydroxyl groups, good yields of substituted oligoethylene glycols were also obtained in several instances.

## Experimental Section

IR spectra were obtained with a Perkin-Elmer Model 267 infrared spectrophotometer and are given in reciprocal centimeters. $^1$H NMR spectra were measured with a Varian EM-360A spectrometer in deuteriochloroform, and chemical shifts are reported in parts per million ($\delta$) downfield from tetramethylsilane. Mass spectra were obtained with a Hewlett-Packard 5595B GC/MS. Elemental analysis was performed by Galbraith Laboratories, Inc., of Knoxville, TN.

Unless specified otherwise, reagent grade reactants and solvents were obtained from chemical suppliers and used as received. The THP$(OCH_2CH_2)_n$Cl with $n$ = 1–3 were prepared from the corresponding chloro alcohols by literature procedures.[27,28]

**(±)-2,3-Octanediol.** A mixture of *trans*-2-octene (5.00 g, 0.046 mol), formic acid (55 mL), and 30% $H_2O_2$ (3.8 mL) was stirred for 24 h at room temperature. After evaporation of the excess acid in vacuo, the residue was refluxed for 1 h with 40 mL of 3 N KOH in EtOH. The solvent was evaporated in vaccuo, and the residue was acidified with 3 N HCl and extracted with $Et_2O$ (3 × 50 mL). The combined organic layers were washed with water, dried ($MgSO_4$), and evaporated in vacuo to give 5.60 g (86%) of white, waxlike solid: mp 45–46 °C (pentane); IR (deposit on NaCl plate) 3280 (OH); $^1$H NMR $\delta$ 0.65–2.7 (m, 14), 3.15–4.0 (m, 4). Anal. Calcd for $C_5H_{18}O_2$: C, 65.17; H, 12.41. Found: C, 65.54; H, 12.48.

**General Method for the Preparation of Functionalized Oligoethylene Glycols.** To a solution of 4-[(benzyloxy)methyl]-3,6-dioxa-1,8-octanediol (2.70 g, 0.010 mol), THPOC$H_2CH_2$Cl (10.00 g, 0.060 mol), and tetrabutylammonium hydrogen sulfate (0.30 g, 0.88 mmol) was added dropwise aqueous 50% NaOH (0.20 mol), and the two-phase mixture was stirred vigorously and heated at 65 °C for 3 days under nitrogen. The reaction mixture was taken up into $CH_2Cl_2$ and washed with water. The organic layer was dried ($MgSO_4$) and filtered through a layer of silica gel with EtOAc as eluent. Unreacted THPO$CH_2CH_2$Cl and a volatile elimination product were removed in vacuo. The pure bis(tetrahydropyranyl) intermediate was obtained by column chromatography on silica gel with EtOAc as eluent and was readily deprotected by addition to 60 mL of MeOH–$CH_2Cl_2$ (1:1), which contained 0.6 mL of concentrated aqueous HCl, and stirring for 2 h at room temperature. After addition of $NaHCO_3$ (2.9 g) to neutralize the acid, the solvent was removed in vacuo. EtOAc was added to the residue, and the inorganic salts were filtered. Solvent was removed from the filtrate in vacuo to give pure 7-[(benzyloxy)methyl]-3,6,9,12-tetraoxa-1,14-tetradecanediol (entry 2, Table I).

**5-Benzyl-3,7-dioxa-1,9-nonanediol** (entry 4): colorless liquid; IR (neat) 3380 (OH), 1120 and 1065 (C–O); $^1$H NMR $\delta$ 2.0–3.2 (m, 5), 3.4–3.95 (m, 12), 7.22 (s, 5). Anal. Calcd for $C_{14}H_{22}O_4$: C, 66.12; H, 8.72. Found: C, 65.76; H, 8.66.

**7(*S*),8(*S*)- and 7(*R*),8(*R*)-Bis[(benzyloxy)methyl]-3,6,9,12-tetraoxa-1,14-tetradecanediol** (entry 10): colorless, hygroscopic, viscous liquid; IR (neat) 3440 (OH), 1100 (C–O); $^1$H NMR $\delta$ 3.33 (s, 2), 3.35–3.95 (m, 22), 4.51 (s, 4), 7.33 (s, 10). Anal. Calcd for $C_{26}H_{38}O_8 \cdot 0.5H_2O$: C, 64.04; H, 8.06. Found: C, 63.79; H, 8.14.

***meso*-7,8-Diphenyl-3,6,9,12-tetraoxa-1,14-tetradecanediol** (entry 11): colorless hygroscopic oil; IR (neat) 3420 (OH), 1130–1070 (C–O); $^1$H NMR $\delta$ 2.85–3.8 (m, 18), 4.47 (s, 2), 7.28 (s, 10). Anal. Calcd for $C_{22}H_{30}O_6 \cdot 0.25H_2O$: C, 66.90; H, 7.78. Found: C, 66.68; H, 7.92.

**2,2-(7′-Hydroxy-2′,5′-dioxaheptyl)-4,7-dioxa-9-nonanol** (entry 12): colorless, extremely hygroscopic, viscous oil; IR (neat) 3400 (OH), 1135–1060 (C–O); $^1$H NMR $\delta$ 0.95 (s, 3), 3.05–3.90 (m, 33); MS 385 ($M^+ + 1$). Anal. Calcd for $C_{17}H_{36}O_9 \cdot 1.5H_2O$: C, 49.62; H, 9.55 Found: C, 49.30; H, 9.55.

**1-[(2′-Tetrahydropyranyl)oxy]-5-[(triphenylmethyl)-oxy]-3-oxapentane** (entry 13): colorless oil; IR (neat) 1125, 1075, 1030 (C–O); $^1$H NMR $\delta$ 1.3–2.0 (m, 6), 3.25 (t, 2), 3.45–4.05 (m, 8), 4.67 (br s, 1), 7.15–7.65 (m, 15); MS 432 ($M^+$). Anal. Calcd for $C_{28}H_{32}O_4$: C, 77.75; H, 7.46. Found: C, 78.04; H, 7.49.

**4-Methyl-5-pentyl-3,6-dioxa-1,8-octanediol** (1): colorless liquid; IR (neat) 3400 (OH), 1120 (C–O); $^1$H NMR $\delta$ 0.65–1.7 (m, 14), 3.1–4.0 (m, 12). Anal. Calcd for $C_{12}H_{26}O_4$: C, 61.51; H, 11.18. Found: C, 61.34; H, 11.41.

**Mixture of 1,5-dihydroxy-4-methyl-3-oxadecane (2) and 4-(1′-hydroxyethyl)-3-oxa-1-nonanol (3)**: colorless liquid; $^1$H NMR $\delta$ 0.65–1.75 (m, 14), 3.14–4.25 (m, 8).

**8-Hydroxy-9-(3′-hydroxy-1′-oxapropyl)hexadecane (4)**: colorless liquid; bp 166–168 °C (0.35 Torr); IR (neat) 3380 (OH); $^1$H NMR $\delta$ 0.6–1.8 (m, 30), 2.9–4.3 (m, 8). Anal. Calcd for $C_{18}H_{38}O_3$: C, 71.47; H, 12.66. Found: C, 71.14; H, 12.87.

**7,7-Diphenyl-3,6-dioxaheptanol (5)**: colorless hygroscopic oil; IR (neat) 3420 (OH), 1130–1060 (C–O); $^1$H NMR $\delta$ 2.70 (br s, 1), 3.35–3.8 (m, 8), 5.40 (s, 1), 7.32 (br s, 10); MS 272 ($M^+$). Anal. Calcd for $C_{17}H_{20}O_3 \cdot 0.5H_2O$: C, 72.57; H, 7.52. Found: C, 72.38; H, 7.82.

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