

crystalline material formed was collected by filtration; mp 150–152 °C; MS, *m/e* 450 (95), 270 (100).

The above diester was dissolved in hot ethanol (300 mL), to which NaOH solution (5 g in 20 mL) was added, and the mixture was refluxed continually for 8 h. The solvent was then evaporated, and the residue was redissolved in water (750 mL) and acidified with HOAc to give a white solid. The diacid, after collection by filtration and drying in vacuum, was decarboxylated in boiling ethanolamine (100 mL). The hot mixture was poured into ice water and extracted twice with dichloromethane (200 mL). Evaporation of the organic phase afforded the tarry dipyrromethane 6, which was then formylated via the Vilsmeier reaction without purification. POCl₃ (3 mL) was added dropwise to a stirred, cold solution of 6 (5 g) in DMF (50 mL) at 0–5 °C. The mixture was allowed to stir at room temperature under nitrogen overnight. At the end of the period, water (200 mL) was added and the mixture extracted several times with CH₂Cl₂ until the organic layer was almost colorless. NaOH solution (10%) was added dropwise to the aqueous layer until complete precipitation was obtained. The light brown crystalline material was collected by filtration and recrystallized from 95% ethanol to give white needles (3.5 g, 60% yield): mp 210–212 °C; NMR δ 1.10 (6 H, t, Et), 1.75 (6 H, s, Me), 2.60 (4 H, q, Et), 5.45 (1 H, s, CH), 7.1 (5 H, m, Ph), 9.25 (2 H, s, CHO), 9.55 (2 H, br, NH); *m/e* 362 (100), 226 (50). Anal. Calcd for C₂₃H₂₆N₂O₂: C, 76.21; H, 7.23. Found: C, 75.95; H, 7.20.

1,8-Bis[5-(2,8,13,17-tetraethyl-3,7,12,18-tetramethyl)porphyrinyl]anthracene (1). A solution of the 5,5'-unsubstituted 4c (634 mg, 1 mmol) and the [bis(methoxymethyl)dipyrromethene 7 (794 mg, 2 mmol) in benzene (100 mL) was heated to reflux for 1 h. Tetrachloro-*o*-benzoquinone (1 g) was added and the solution was stirred at room temperature for 1/2 h. TLC (silica gel/chloroform) revealed that two porphyrins were produced: the one migrated near the solvent front was etioporphyrin II and the other, which exhibited a very faint fluorescence, was the diporphyrin 1. To facilitate separation of 1 from the remaining dark-colored waste, the mixture, after removal of the benzene solvent, was heated in dichloromethane with methanolic copper(II) acetate. The red copper porphyrins were isolated by chromatography on silica gel (CH₂Cl₂). Copper was then removed by shaking the eluent with 12 N sulfuric acid. After neutralization and back extraction the two demetalated porphyrins were separated by column chromatography (silica gel/CH₂Cl₂): yield, 80 mg of 1 and 150 mg of etioporphyrin II. NMR of 1: δ 1.27 (12 H, t, Et), 1.66 (12 H, t, Et), 1.87 (12 H, s, Me), 3.17 (12 H, s, Me), 3.38 (8 H, q, Et), 3.9 (8 H, 2 q, Et), 7.58 (2 H, t, 2, 7H-an), 7.71 (2 H, t, 3,6H-an), 8.50 (2 H, d, 4,5H-an), 8.90 (1 H, s, 10H-an), 8.95 (4 H, s, meso-H), 9.00 (1 H, s, 9H-an), 9.34 (2 H, s, meso-H), -4.98 (4 H, br, NH); MS, *m/e* 1131 (89), 1130 (100), 565 (81); high-resolution MS, 1130.6670 (C₇₈H₈₂N₆); UV-vis λ_{max} (ε_{mM}) 625 nm (4.0), 572 (9.0), 537 (10), 503 (22), 394 (232). Anal. Calcd: C, 82.79; H, 7.30; N, 9.90. Found: C, 82.81; H, 7.41; N, 9.85.

5-Phenyl-2,8,13,17-tetraethyl-3,7,12,18-tetramethylporphine (8). Phenylidipyrromethane 6 (470 mg, 1.5 mmol) and dipyrromethene 7 (650 mg, 1.55 mmol) were dissolved and heated to reflux in benzene (80 mL) for 1 h. After cooling, tetrachloro-*o*-benzoquinone (200 mg) was added to complete oxidation. The products were chromatographed on a silica gel column with dichloromethane/hexane mixture as eluent to yield 160 mg (17.8%) of the desired monophenylporphyrin. A small amount (30 mg) of etioporphyrin II, which was eluted first, was also obtained. 8: NMR δ 1.81 (6 H, t, Et), 1.90 (6 H, t, Et), 2.45 (6 H, s, Me), 3.69 (6 H, s, Me), 4.05 (8 H, 2 q, Et), 7.78 (3 H, m, 3,4,5H-Ph), 8.05 (2 H, d, 2, 6H-Ph), 9.96 (1 H, s, meso-H), 10.15 (2 H, s, meso-H), -3.3 (2 H, br, NH); MS *m/e* 554 (100), 277 (34); UV-vis λ_{max} (ε_{mM}) 626 nm (2.5), 559 (6.7), 534 (7.0), 501 (15.5), 402 (188). Anal. Calcd for C₃₈H₄₂N₄: C, 82.27; H, 7.63; N, 10.10. Found: C, 82.14; H, 7.71; N, 10.17.

Octaethylporphyrin from the [(Methoxymethyl)dipyrromethene Condensation. [5,5'-Bis(bromomethyl)-3,4,3',4'-tetraethyl-2,2'-dipyrromethene hydrobromide]¹⁸ (12 g) in methanol (200 mL) was heated under reflux for 30 min. The

mixture was evaporated to dryness and the residue triturated with ether/methanol (5:1). The resultant [(methoxymethyl)dipyrromethene (7.5 g) was used without further purification to condense with (3,4,3',4'-tetraethyl-2,2'-dipyrromethane)⁸ in hot benzene. After oxidation by *o*-chloroanil, octaethylporphyrin was isolated in 28% yield: NMR δ 1.09 (24 H, t, Et), 2.40 (16 H, q, Et), 10.1 (4 H, s, meso-H), -3.88 (2 H, br, NH); mp 324 °C (lit.¹⁹ mp 324–325 °C). This porphyrin was identical in every respect with an authentic sample of OEP.

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Registry No. 1, 87597-38-4; 2, 34824-75-4; 3, 4949-58-0; 4a, 87597-39-5; 4b, 87597-40-8; 4c, 87597-41-9; 5, 87597-42-0; 6, 87597-43-1; 7, 87597-44-2; 8, 87597-45-3; (3,3'-diethyl-4,5,4',5'-tetramethyl-2,2'-dipyrromethene hydrobromide, 66145-65-1; [5,5'-bis(bromomethyl)4,4'-dimethyl-3,3'-diethyl-2,2'-dipyrromethene hydrobromide, 87597-46-4; benzaldehyde, 100-52-7; α,α-[5,5'-bis(ethoxycarbonyl)-4,4'-diethyl-3,3'-dimethyl-2,2'-dipyrromethene], 87597-47-5; α,α-[5,5'-dicarboxy-4,4'-diethyl-3,3'-dimethyl-2,2'-dipyrromethene], 87597-48-6; [5,5'-bis(bromomethyl)-3,4,3',4'-tetraethyl-2,2'-dipyrromethene hydrobromide, 87597-49-7; [5,5'-(methoxymethyl)-3,4,3',4'-tetraethyl-2,2'-dipyrromethene hydrobromide, 87597-50-0; (3,4,3',4'-tetraethyl-2,2'-dipyrromethane, 65858-34-6; octaethylporphyrin, 2683-82-1.

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Poly(ethylene glycol) Ethers as Recoverable Phase-Transfer Agents in Permanganate Oxidations

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There has been much recent interest in poly(ethylene glycols) (PEG'S) as inexpensive, nontoxic, thermally stable phase-transfer agents (PTA's).¹⁻³ In our work we have demonstrated the added feature of recovery of the PEG by precipitation.¹ One problem with PEG's as PTA's is the difficulty in controlling PEG partitioning between aqueous and organic phases. In general, PEG partitions almost totally in favor of water relative to the organic layer (e.g., 99.9% PEG in water vs. benzene); an exception is methylene chloride, where the partitioning shifts dramatically in the other direction (75–99% PEG in methylene chloride vs. water, depending on concentration).¹ This difficulty can be avoided by conducting reactions without an aqueous phase (solid-liquid phase transfer) or by preparing derivatized PEG's, providing control of partitioning between aqueous and organic layers; here we describe an approach to the latter solution using PEG alkyl ethers.

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Table I. Synthetic, Partitioning, and Kinetic Results for PEG Ethers

PEG ether	remaining RBr (% w/w) ^a	% subst ^c		partitioning (% in C ₆ H ₆) ^e	oxidation, ^f k, min ⁻¹
		NMR ^b	HPLC		
C4-1500-C4	<0.1	64		14	0.008 ± 0.001
C6-1500-C6	<0.1	61		84	
C18-6000-C18	0.2	79 ⁱ	90 ^d	g	0.04 ± 0.01
C18-750-Me	0.7	100 ⁱ	94	108	0.018 ± 0.001
C18-1900-Me	0.5	92 ^{i,j}	88	39	0.058 ± 0.006
C18-5000-Me	0.4	91 ⁱ	81	37	0.016 ± 0.000
C8-5000-Me ^k	0.2			12	0.008 ± 0.002
C4-5000-Me ^k	<0.1			13	<0.002
PEG 6000				<1	<0.0002 ^h

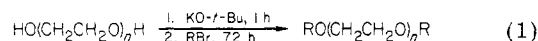
^a GLC. ^b From alkyl H/PEG H. ^c Percent of hydroxyl termini substituted. ^d Percent of total sites; 9% mono- and 86% disubstituted. ^e As compared to water; determined by solvent removal and weighing. ^f Potassium permanganate with 1-octene, as described in text. ^g Emulsification prevented phase separation. ^h Reaction with no PTA gave a similar result. ⁱ Adjusted for contribution from alkyl bromide. ^j Approximately 100% from elemental analysis. ^k Analytical measures of percent substitution are highly inaccurate here and not reported.

It is important to note that the absence of an aqueous phase can itself cause problems. For example, Lee used a mixture of methylated glymes as the PTA in the oxidation of alkenes in benzene with solid permanganate; if aqueous permanganate were used, no phase transfer of permanganate was accomplished.^{2b} The absence of water in this case interferes in that manganese apparently is not fully reduced in an anhydrous environment.

In the present work we describe the preparation of several PEG ethers, determine their partitioning between water and benzene, and examine their utility as PTA's in permanganate oxidation of alkenes in water-benzene. Also, since partitioning of PEG between water and methylene chloride appears favorable, we have examined alkene oxidation in this system using the parent PEG as the PTA, taking advantage of PEG's recoverability to facilitate product isolation.

Results and Discussion

The ethers shown in Table I were synthesized according to eq 1 by using benzene as solvent. Our abbreviated



nomenclature system (Table I) presents the number of carbons of the alkyl group capping one PEG terminus followed by the molecular weight of PEG, followed in turn by the number of carbons of the alkyl group capping the remaining PEG terminus; thus C18-750-Me represents the octadecyl methyl ether of PEG of 750 g/mol.

We determined the pseudo-first-order rate constant for reaction of a five-fold excess of the alkoxide of PEG-1900 monomethyl ether with *n*-octyl bromide in benzene by following the disappearance of octyl bromide with gas chromatography. Duplicate reactions gave $k_1 = 0.36 \pm 0.02 \text{ h}^{-1}$ (correlation coefficients were 0.99) and $k_2 = 5.1 \text{ M}^{-1} \text{ h}^{-1}$ (for [PEG-O⁻] of 0.070 M). For our preparative runs [PEG-O⁻] ≈ [RBr] ≈ 0.022 M, and we calculate the half-life as approximately 9 h; thus our reaction time of 72 h for the preparative runs is about 8 half-lives.

Also contained in Table I are the results of partitioning the PEG ethers between benzene and water. These data were obtained by evaporating the solvent and weighing the residue remaining. It is obvious that the PEG ethers do, as expected, partition more strongly into the benzene layer of a benzene-water system. One might suspect that a relationship would exist between the relative sizes of alkyl and PEG portions of the ether and the preference for benzene as opposed to water. However, comparison of the percent ether partitioned into the benzene layer of a benzene-water system with the ratio (no. alkyl car-

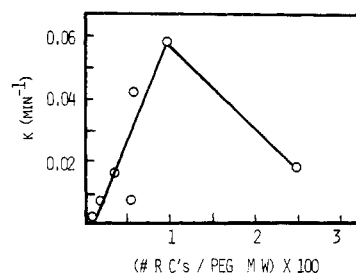


Figure 1. Relationship between ratio of number of alkyl carbons to PEG molecular weight and the rate constant for phase-transfer-catalyzed oxidation of octene with RO-PEG-OR and KMnO_4 .

bons)/(PEG molecular weight) shows only a rough correlation (correlation coefficient = 0.87). Apparently, there is no simple relationship controlling the partitioning behavior of these ethers.

Since significant fractions of the PEG ethers are partitioned into benzene relative to water, we would expect these ethers to transfer salts from water into benzene. This expectation is confirmed by the observation that addition of PEG ether to a permanganate-water-benzene system produces a purple benzene layer; the parent PEG produces no observable permanganate transfer. The potential of PEG ethers as liquid-liquid phase-transfer catalysts was determined by comparing the rate of octene oxidation in benzene by aqueous potassium permanganate in the presence of the various PEG ethers, Table I. Pseudo-first-order rate constants were determined by following the disappearance of octene by GC in the presence of an excess of permanganate; the mass of the PTA was the same in all cases. Reactions were followed for 1 to 2 half-lives and exhibited correlation coefficients of 0.93 or better; the average correlation for 12 rate determinations is 0.97. All the PEG ethers except C4-5000-Me permit effective oxidation of octene in benzene with aqueous permanganate; unsubstituted PEG and the glymes^{2b} are ineffective, as is reaction in the absence of catalyst. The rate enhancements observed appear to be controlled by the length of the hydrocarbon portion of the ether relative to the size of the PEG backbone (Figure 1). If the ratio of hydrocarbon to PEG becomes so large that the PEG ether is partitioned mostly to the benzene, the rate is less than when the hydrocarbon to PEG ratio is balanced so that the PEG ether partitions nearly equally between the phases (compare C18-750-Me and C18-1900-Me). On the other hand, as the ratio of hydrocarbon to PEG becomes small and the partitioning favors water, the amount of rate enhancement is decreased (compare C18-5000-Me, C8-5000-Me, and C4-5000-Me). The optimum catalyst is the one that par-

titions approximately equally between the water and benzene. This conclusion is in contrast to that of Starks and Liotta⁴ who propose that the better catalysts are those that more strongly favor the organic layer.

Preparative-scale reaction with the alkyl ethers is effective; reaction of 0.69 g of 1-octene with C18-6000-C18 as catalyst gave 0.47 g of isolated heptanoic acid. Catalyst recovery by precipitation with ethyl ether from benzene solution was complete. Similarly, reaction with the water-methylene chloride system is also preparatively useful with unsubstituted PEG-6000 as the PTA.^{2b} Yields of 70% are easily achieved, and again PTA recovery by precipitation makes product isolation trivial.

In summary, we can conclude that the PEG ethers can be designed to provide effective, recoverable PTA's for water-benzene systems. The parent PEG can be used similarly in a water-methylene chloride system.

Experimental Section

Unless otherwise noted, all reagents were obtained from either Aldrich Chemical Co. or Fisher Scientific Co. and are used without further purification. GC work was performed on a Varian 4600 GC with an FID detector and a 5% SE-30 Chromosorb 60/80 column (9 ft × 0.125 in.). HPLC work was performed on a Perkin-Elmer Series 2 liquid chromatograph with an LDC Model 1107 Refracto-Monitor detector and a Waters μ Bondapak C18 column (30 cm × 3.9 mm). Both the GC and the HPLC were connected with a Varian Vista 401 Data Station. Proton NMR spectra were determined on a Varian EM-360 60-MHz NMR spectrometer.

Synthesis of PEG Ethers. The following preparation is typical: PEG 6000 (10.0 g, 0.00167 mol) was dissolved in 40 mL of dry benzene and added dropwise to a suspension of potassium *tert*-butoxide (10% excess; 0.4 g, 0.00367 mol) in 20 mL of dry benzene under a nitrogen atmosphere. The mixture was allowed to stir at room temperature for 1 h. Octadecyl bromide (2× excess; 2.2 g, 0.00668 mol) was dissolved in 15 mL of dry benzene and added dropwise to the mixture, which was then stirred at room temperature for 72 h. After filtration to remove insoluble salts, the benzene was removed by rotoevaporation. The product was redissolved in methylene chloride and eluted down a short silica gel column (1 in. × 5 in.) with methylene chloride. This removed dissolved salts and some of the unreacted PEG. The eluent was concentrated by rotoevaporation and the PEG ether precipitated by dropwise addition to diethyl ether. Product isolated by precipitation was gummy and difficult to filter. This step served only to remove a portion of the hydrocarbons present. On the basis of the method of Van Alstine,⁵ the product was further purified by chromatography on Sephadex LH-20 gel (Pharmacia) with 5:1 methanol-water as eluent (1 g dissolved in 30 mL of eluent on a 1 × 12 in. column with a flow rate of 0.5 mL/min). The eluent was concentrated by rotoevaporation and dried several hours in vacuo. Product thus isolated was 75-90% substituted with 0.2% (w/w) alkyl bromide contaminant remaining.

Characterization of PEG Ethers. The amount of alkyl bromide remaining in the product was determined by GC by comparing with nonane internal standard. Substitution was determined by NMR (in CDCl₃) by measuring the ratio of alkyl hydrogens (δ 1.30) to ether hydrogens (δ 3.75). Substitution was also determined for C18 ethers by HPLC (C18 column). Eluent was 65:35 acetonitrile-methanol except for PEG-6000-(C18)₂, where 35:65 acetonitrile-methanol was used. Flow was 2.0 mL/min; 5-10 μ L of 5% sample was injected.

Kinetics of PEG Ether Synthesis. PEG-1900 monomethyl ether (1.00 g, 0.000526 mol) in 4 mL of dry benzene was added to a suspension of KO-*t*-Bu (10% excess; 0.065 g, 0.00058 mol) in 2 mL of dry benzene. This mixture was stirred at 35 °C for 1 h. One-fifth of the molar equivalent of octyl bromide (0.020

g, 0.000105 mol) in 1.5 mL of dry benzene was added. Samples were periodically withdrawn, and the disappearance of octyl bromide was followed by GC.

Partitioning of PEG Ethers between Benzene and Water. Typically, 1 mL of a 5% (w/w) solution of PEG ether in benzene was quantitatively prepared in a 1-dram vial. An equal volume of water was added and the vial inverted several times to mix the phases. After settling overnight, a weighed portion of the benzene phase was placed in a second vial. Most of the benzene was evaporated under a stream of nitrogen. The samples were dried in vacuo for several hours and the weight of the PEG ether partitioned into benzene determined. This procedure was complicated by emulsification with C18 ethers.

Kinetic Study of Phase-Transfer-Catalyzed Oxidation of Octene. Reactions were conducted in jacketed reaction vials with stirring at 35 °C. The vial was charged with 7.2 mL of 0.4 M KMnO₄ in 0.5% acetic acid. After the solution was stirred for 10 min, 2.0 mL of 0.36 M octene in benzene containing 0.7 mmol of nonane (internal standard) and 0.08 g of PTA was added. Aliquots were withdrawn, diluted with acetonitrile, and injected on the GC.

Preparative-Scale Oxidation of Octene. A 250-mL reaction flask was charged with 61 mL of 0.4 M KMnO₄ (24.4 mmol) in 0.5% acetic acid. A chilled water bath was used to maintain the temperature below 40 °C as 17 mL of 0.36 M octene in benzene with 0.68 g of PEG-6000-(C18)₂ slowly added. Stirring was continued for 5 h, 50% sulfuric acid was added until the solution was acidic, and sodium bisulfite was added to reduce MnO₂. The phases were separated, and the product was removed by extraction into aqueous base. Neutralization, drying, and rotoevaporation gave heptanoic acid (GC, 59%). A second reaction in methylene chloride with PEG gave a 70% yield.

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Registry No. C₄O(CH₂CH₂O)_nC₄, 31885-97-9; C₄O-(CH₂CH₂O)_nMe, 80730-57-0; C₁₈O(CH₂CH₂O)_nC₁₈, 36493-26-2; C₁₈O(CH₂CH₂O)_nMe, 27252-82-0; C₈O(CH₂CH₂O)_nMe, 27252-82-0; HO(CH₂CH₂O)_nH, 25322-68-3; C₆O(CH₂CH₂O)_nC₆, 27900-79-4; KMnO₄, 7722-64-7; 1-octene, 111-66-0; octadecyl bromide, 112-89-0.

Synthesis of Alkene-Substituted Pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecanes. An Improved Synthesis of 8,11-Dimethylene-pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane

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Substituted pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecanes recently have received considerable attention as intermediates in the synthesis of tricyclopentanoid natural products.¹⁻³ In our studies of the synthesis and chemistry of new substituted pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecanes,⁴⁻⁹

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