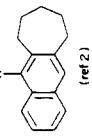
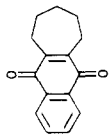
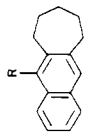
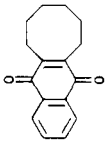
ix		8.49	85[a]	109–10	1.69–1.73 (m, 4 H), 1.82–1.88 (m, 2 H), 2.92–2.96 (m, 4 H), 5.17 (s, 1 H, Ar OH), 7.23 (s, 1 H, Ar H), 7.38–7.44 (m, 2 H, Ar H), 7.67–7.71 (m, 1 H, Ar H), 7.99–8.01 (m, 1 H, Ar H)		75[f]	100–02	1.56–1.61 (m, 4 H), 1.84–1.90 (m, 2 H), 2.85–2.88 (m, 4 H), 7.66–7.71 (m, 2 H, Ar H), 8.05–8.08 (m, 2 H, Ar H)	Calcd. for $C_{15}H_{14}O_2$: C, 79.65; H, 6.19. Found: C, 79.45; H, 6.26.
x		8.51	84[a]	99–100	1.32–1.47 (m, 4 H), 1.72–1.76 (m, 4 H), 2.90–2.97 (m, 4 H), 5.17 (s, 1 H, Ar OH), 7.26 (s, 1 H, Ar H), 7.39–7.44 (m, 2 H, Ar H), 7.69–7.72 (m, 1 H, Ar H), 8.04–8.06 (m, 1 H, Ar H)		84[f]	79–80	1.48–1.50 (m, 4 H), 1.55–1.74 (m, 4 H), 2.80–2.83 (m, 4 H), 7.69–7.71 (m, 2 H, Ar H), 8.08–8.10 (m, 2 H, Ar H)	Calcd. for $C_{16}H_{16}O_2$: C, 80.0; H, 6.67. Found: C, 79.90; H, 6.71.

[a] a = formate hydrolysis with Al_2O_3. [b] b = formate hydrolysis with aq. Na_2CO_3. [f] f = oxidation with Fremy's salt. [s] s = oxidation with salcomine. [b] Chemical shift of formate proton (δ) (R = OCHO).

added a methanolic solution of the naphthol (0.1 mmol). The solution was stirred at 0 °C for 2–4 h and then extracted with dichloromethane (3 × 10 mL). The organic layer was washed with water, dried (ahydrous $MgSO_4$), and concentrated under reduced pressure. The residue was purified with use of the chromatotron to give the quinone.

(ii) Using Salcomine. The naphthol (0.1 mmol) was dissolved in anhydrous tetrahydrofuran (4 mL), and salcomine (0.05 mmol) was added to it. It was stirred under oxygen atmosphere for 3–4 h at room temperature. It was then concentrated under reduced pressure and passed through a small bed of Florisil using dichloromethane or dichloromethane–methanol (95:5) (for polar quinones) as the solvent. The eluted solvent was concentrated, and the residue was finally purified by chromatotron to give the pure quinone.

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Registry No. i (R = CHO), 66-77-3; i (R = OCHO), 1988-19-8; i (R = OH), 90-15-3; ii (R = CHO), 66-99-9; ii (R = OCHO), 1988-18-7; ii (R = OH), 135-19-3; iii (R = CHO), 93831-85-7; iii (R = OCHO), 98170-01-5; iii (R = OH), 98170-09-3; iv (R = CHO), 98243-95-9; iv (R = OCHO), 98170-02-6; iv (R = OH), 98170-10-6; iv (naphthoquinone), 98170-14-0; v (R = CHO), 96301-83-6; v (R = OCHO), 98170-03-7; v (R = OH), 27532-59-8; v (naphthoquinone), 26386-96-9; vi (R = CHO), 82584-15-4; vi (R = OCHO), 98170-04-8; vi (R = OH), 50703-94-1; vi (naphthoquinone), 4923-66-4; vii (R = CHO), 96301-88-1; vii (R = OCHO), 98170-05-9; vii (R = OH), 98170-11-7; vii (naphthoquinone), 52651-48-6; viii (R = CHO), 96301-86-9; viii (R = OCHO), 98170-06-0; viii (R = OH), 98170-12-8; viii (naphtoquinone), 98170-15-1; ix (R = CHO), 96301-84-7; ix (R = OCHO), 98170-07-1; ix (R = OH), 98170-13-9; ix (naphthoquinone), 98170-16-2; x (R = CHO), 96301-85-8; x (R = OCHO), 98170-08-2; x (R = OH), 50703-96-3; x (naphthoquinone), 98170-17-3.

Phosphate Ester Cleavage by Functionalized Quaternary Phosphonium Surfactants

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There have been numerous studies of micellar catalysis of phosphate ester hydrolysis involving functionalized quaternary ammonium surfactants.[1] Herein, we report such a study with the first examples of functionalized quaternary phosphonium analogues.

Hydroxyl-functionalized surfactants **1** were evaluated as potential turnover catalysts for the basic hydrolysis of phosphate ester **4** according to eq 1–4. If eq 3 and 4 are faster than the formation of **5**, **1** would indeed function as turnover catalysts. The catalytic abilities of **1a** and

$$\underset{\mathbf{1}}{RPh_2P^+CH_2CH_2OH,Br^-} \qquad \underset{\mathbf{2}}{RPh_2P^+C_3H_7\text{-}n,Br^-}$$

$$\underset{\mathbf{3}}{RPh_2P^+CH{=}CH_2,Br^-}$$

a, R = 4-n-$C_{12}H_{25}C_6H_4$ **b**, R = n-$C_{12}H_{25}$

analogues **2a** and **3a** were studied first in 0.01 M NaOH; pseudo-first-order rate constant (k_ψ) vs. concentration profiles (not shown) are summarized in Table I. With **1a**

(1) For a summary and examples, see: Moss, R. A.; Ihara, Y. *J. Org. Chem.* **1983**, *48*, 588 and references therein.

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Table I. Hydrolysis of Ester 4[a] in 0.01 M NaOH[b] at 25 °C

surfactant concn, 10^3 M	k_ψ,[c] s^{-1} 1a	2a	3a
0.025		0.0196	
0.050	0.291	0.0408	
0.10	1.01	0.0780	0.50[d]
0.25	1.87	0.202	0.168
0.50	2.08	0.222	0.171
1.5	2.20	0.209	
2.5	2.09	0.158	
10	1.52		

[a] [4] = 1.0×10^{-5} M. [b] Contained 1.3% (v/v) 1,4-dioxane. [c] Averages of duplicate runs; average deviations ≤6% unless noted otherwise. Without surfactant, k_ψ = 0.0034 s^{-1}. [d] Average deviation 14%.

Table II. Hydrolysis of Ester 4[a] at pH 10[b] and 25 °C

time delay,[c] h	$10^2 k_\psi$,[d] s^{-1} 1a	2a	3a
0	3.34	0.470	0.546
0.17	3.20	0.465	0.869
0.33			1.05
1.0			1.67
3.0	2.99		1.89
5.0			2.10
8.0			1.86
24.0	2.78		1.52

[a] [4] = 1.0×10^{-5} M and [surfactant] = 0.001 M. [b] 0.0125 M borate buffer (μ = 0.043) containing 1.3% (v/v) 1,4-dioxane. [c] See text. [d] Averages of at least duplicate runs; average deviations ≤4%. Without surfactant, $k_\psi = 1.5 \times 10^{-4}$ s^{-1}.

and **2a**, the k_ψ's pass through maxima as has been observed with related quaternary ammonium systems.[2] At a given concentration, $k_\psi^{1a} > k_\psi^{2a}$, which suggests the involvement of 1′ in nucleophilic attack on **4** (eq 2). Resultant intermediate **5** likely undergoes ElcB elimination to **3** and **6** (eq 3) faster than its formation.[3] The k_ψ^{3a}'s indicate that **1a** does not function as a turnover catalyst since they are uniformly less than the corresponding k_ψ^{1a}'s and are about

$$1 + {}^-OH \rightleftharpoons \underset{1'}{RPh_2P^+CH_2CH_2O^-},Br^- + H_2O \quad (1)$$

$$1' + p\text{-}NO_2C_6H_4OPO(OPh)_2 \xrightarrow[4]{} RPh_2P^+CH_2CH_2OPO(OPh)_2 + p\text{-}NO_2C_6H_4O^- \quad (2)$$

$$\underset{5}{} \xrightarrow[H_2O]{{}^-OH} 3 + {}^-OPO(OPh)_2 \quad (3)$$

$$\underset{6}{} \quad 3 + H_2O \xrightarrow{{}^-OH} 1 \quad (4)$$

the same as the k_ψ^{2a}'s. Thus, eq 4 cannot be faster than eq 2. In fact, **3a** did not yield **1a** under the reaction conditions but instead suffered complex decomposition initiated by attack of ^-OH at P[4] which indeed complicated the determination of k_ψ^{3a} (see Experimental Section).

With 0.005 M **1b**, **2b**, and **3b** in 0.01 M NaOH, k_ψ = 0.50, 0.050, and 0.057 s^{-1}, respectively. Therefore, **1b**, like **1a**, does not function as a turnover catalyst. With 0.001 M $Ph_3P^+CH_2CH_2OH,Br^-$ (**7**) in 0.01 M NaOH, k_ψ = 0.0036 ± 0.0001 s^{-1}, which is comparable to k_ψ in 0.01 M NaOH alone, 0.0034 ± 0.0001 s^{-1}. Thus, the catalytic effects of **1a** and **1b** are due to their micellar behavior.

The catalytic abilities of 0.001 M **1a**, **2a**, and **3a** were also studied at pH 10 (borate buffer), and k_ψ's are summarized in Table II. In these reactions various time delays were used between the preparation of the surfactant–buffer solution and the addition of **4**. With no delay, $k_\psi^{1a} \gg k_\psi^{2a} \sim k_\psi^{3a}$ as found at pH 12. Therefore, **1a** does not act as a turnover catalyst at pH 10 either. However, **3a** undergoes Michael-like addition of H_2O to give **1a** (eq 4) rather than attack at P.[4] Indeed, k_ψ^{3a} increased with the length of the delay through 5 h, reflecting the **3a** → **1a** conversion[5] and the latter's greater catalytic activity. But note that the **3a** system does not attain the full kinetic advantage of **1a**, which is probably due to partial conversion of resultant **1a** into $(RPh_2P^+CH_2CH_2)_2O,2Br^-$ by its addition to **3a** and to some decomposition of **1a** and **3a**.[4] Consistent with this is the decrease in k_ψ^{1a} with an increase in the delay.

In 0.01 M NaOH the catalytic abilities of **1a** and **1b** are comparable to those of $RMe_2N^+CH_2CH_2OH,Br^-$ (**8**: **a**, R = n-$C_{12}H_{25}$; **b**, R = n-$C_{16}H_{33}$; **c**, R = n-$C_{18}H_{37}$) in the hydrolysis of **4**. Bunton and Ionescu obtained[2] maximum k_ψ values of 0.38 and 1.5 s^{-1} with **8a** and **8b**, respectively, at 25 °C.[6]

The Hammett σ_p constants for Me_3P^+ and $MePh_2P^+$ are 0.95[7a] and 1.01,[7b] respectively, and that of Me_3N^+ is 0.86.[7c] Thus, the substitution of Ph for Me does not significantly alter the electron-withdrawing ability of a phosphonium substituent, and consequently, **1a** and **1b** should have pK_a's close to those of **8**. There is considerable uncertainty, however, in the pK_a of micellar **8**; values of 9.5[8a] and ca. 12.4[2] have been reported for **8b**, and ca. 10.5 for **8c**.[8b] The pK_a of choline is 12.8,[8c] and those of micellar **1a** and **1b** should be lower due to electrostatic effects.

Overall, there is no catalytic advantage of the quaternary phosphonium surfactants **1a** and **1b** over analogous quaternary ammonium systems. The inability of **1a** to function as a turnover catalyst at pH 10 derives primarily from the slow rate of eq 4.

Experimental Section

General Procedures. ^1H NMR spectra were recorded at 270 MHz with Me_4Si as internal standard in $CDCl_3$. Fast atom bombardment (FAB) mass spectra were obtained on a Kratos MS-50 triple analyzer spectrometer at the Midwest Center for Mass Spectrometry at the University of Nebraska–Lincoln, and

(2) Bunton, C. A.; Ionescu, L. G. *J. Am. Chem. Soc.* **1973**, *95*, 2912.

(3) (a) The formation of an analogue of **5**, n-$C_{16}H_{33}Me_2N^+CH_2CH_2OPO(OPh)_2$, from **4** and n-$C_{16}H_{33}Me_2N^+CH_2CH_2OH,Br^-$ under similar conditions has been demonstrated (Bunton, C. A.; Gan, L. H.; Hamed, F. H.; Moffat, J. R. *J. Phys. Chem.* **1983**, *87*, 336). (b) In NaOEt–EtOH at 25 °C, the second-order rate constant (k_2) for elimination of $^-OPO(OEt)_2$ from $PhSO_2CH_2CH_2OPO(OEt)_2$ is over 1.5×10^3 times greater than that for elimination of ^-OPh from $PhSO_2CH_2CH_2OPh$ (Marshall, D. R.; Thomas, P. J.; Stirling, C. J. M. *J. Chem. Soc., Chem. Commun.* **1975**, 940). Since k_2 = 2 M^{-1} s^{-1} for $Ph_3P^+CH_2CH_2OPh,Br^-$ in NaOH–H_2O at 25 °C (Crosby, J.; Stirling, C. J. M. *J. Chem. Soc. B* **1970**, 679), that for $Ph_3P^+CH_2CH_2OPO(OEt)_2,Br^-$ is estimated to be 3×10^3 M^{-1} s^{-1}, and k_2 for **5** should be similar. Therefore, in 0.01 M NaOH, the pseudo-first-order rate constant (k_1) for **5** is at least 30 s^{-1} since [^-OH] > 0.01 M in the micelle Stern layer (Bunton, C. A.; Hong, Y. S.; Romsted, L. S. In "Solution Behavior of Surfactants–Theoretical and Applied Aspects"; Mittal, K. L., Fendler, E. J., Eds.; Plenum Press: New York; 1982; Vol. II, p 1137).

(4) Jaeger, D. A.; Bolikal, D., to be published.

(5) The rate constant was not measured because **1a** and **3a** have near identical UV spectra.

(6) Surfactants **8** have no potential as turnover catalysts according to reactions analogous to eq 1–4. In NaOEt–EtOH at 25 °C, k_2 for $Me_3N^+CH_2CH_2OPh,Br^-$ is ca. 5×10^{-9} times less than that for $Ph_3P^+CH_2CH_2OPh,Br^-$ (Crosby, J.; Stirling, C. J. M. *J. Chem. Soc. B* **1970**, 671). Therefore, k_1 for $RMe_2N^+CH_2CH_2OPO(OC_6H_5)_2,Br^-$ in 0.01 M NaOH–H_2O is estimated[3b] to be somewhat greater than 1.5×10^{-7} s^{-1} but certainly dramatically less than k_ψ for **8**.

(7) (a) Tsvetkov, E. N.; Malakhova, I. G.; Kabachnik, M. I. *Zh. Obshch. Khim.* **1978**, *48*, 1230. (b) Schiemenz, G. P. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 595. (c) Jaffé, H. H. *Chem. Rev.* **1953**, *53*, 191.

(8) (a) Begunov, A. V.; Rutkovskii, G. V.; Kuznetsov, S. G. *Zh. Org. Khim.* **1981**, *17*, 1668. (b) Martinek, K.; Levashov, A. V.; Berezin, I. V. *Tetrahedron Lett.* **1975**, *16*, 1275. (c) Haberfield, P.; Pessin, J. *J. Am. Chem. Soc.* **1982**, *104*, 6191.

electron impact (EI) spectra on a VG-ZAB 1F spectrometer. Critical micelle concentrations (cmc) were measured as before.[9] Elemental analyses were performed by Atlantic Microlab, Atlanta, GA.

Solvents and Materials. Tetrahydrofuran (THF) and Et_3N were distilled under N_2 from sodium benzophenone ketyl and KOH, respectively; 1,4-dioxane was purified by a standard procedure[10] and distilled from $LiAlH_4$ under N_2. For kinetic runs, HPLC-H_2O was boiled and degassed with purified N_2. Ester **4**, mp 49–51 °C (lit.[11a] mp 49–51 °C), and **7**, mp 219–220 °C (lit.[11b] mp 217–218.5 °C), were prepared as before.[11] All synthetic procedures were under N_2. Surfactant purity was assessed by TLC (silica gel, 1:19 (v/v) MeOH–$CHCl_3$).

Kinetic Studies. All runs contained 1.0×10^{-5} M **4** and 1.3% (v/v) 1,4-dioxane and were at 25.0 ± 0.1 °C. The reaction of **4** generally was monitored to ≥90% completion by the appearance of p-$NO_2C_6H_4O^-$ at 400 nm (λ_{max}). Rate constants resulted from computer-generated least-squares plots of log ($A_\infty - A_t$) vs. time. Slow reactions were followed with a Carey Model 2300 UV-VIS-NIR spectrophotometer with kinetics accessories. A 1,4-dioxane solution of **4** was added to surfactant–0.01 M NaOH/borate buffer within a 1-cm cuvette containing a star-shaped stirrer, and the resultant solution was intermittently stirred. Fast reactions were follwed with a Durrum Model D150 stopped-flow spectrophotometer. One syringe held 0.02 M NaOH and the other 4–1,4-dioxane–surfactant–H_2O prepared just before the start of a reaction. All runs except those with **3** in 0.01 M NaOH gave good first-order kinetics ($r > 0.999$); A_∞ was determined by experiment. For the latter ($r > 0.997$), decomposition[4] was noted beyond ca. 90% completion, which necessitated calculation[12] of A_∞. Carbonate-free NaOH and 0.0125 M borate buffer (pH 10, $\mu = 0.043$) solutions were prepared by conventional procedures.

(4-Dodecylphenyl)diphenyl(2-hydroxyethyl)phosphonium Bromide (1a). A mixture of 4.3 g (10 mmol) of 4-n-$C_{12}H_{25}C_6H_4PPh_2$[13] and 2.5 g (20 mmol) of $BrCH_2CH_2OH$ (Aldrich) in 10 mL of $MeNO_2$ was degassed (N_2) for 5 min and then held at 80 °C for 24 h. The reaction mixture was concentrated to 3 mL and added to 250 mL of Et_2O. A light yellow, viscous oil that separated at −10 °C was chromatographed on a 3.0 × 50 cm column of silica gel packed in $CHCl_3$. In order, the following were used for elution: 200 mL each of $CHCl_3$, 1:9 (v/v) Et_2O–$CHCl_3$, and 1:1 (v/v) Et_2O–$CHCl_3$ and 500 mL of 1:19 (v/v) MeOH–$CHCl_3$. The surfactant eluted with the last solution, and it was rechromatographed under the same conditions to give 3.0 g (55%) of **1a** as a light yellow oil: ^1H NMR δ 7.46 –7.81 (m, 14 H, Ar H), 5.24 (br s, 1 H, OH), 4.06 (d of t, $J_{P,H}$ = 17.6 Hz, $J_{H,H}$ = 5.9 Hz, 2 H, CH_2O), 3.77 (d of t, $J_{P,H}$ = 12.5 Hz, $J_{H,H}$ = 5.9 Hz, 2 H, CH_2P), 2.71 (t, J = 7.7 Hz, 2 H, CH_2Ar), 1.64 (br m, 2 H, CH_2CH_2Ar), 1.26 (m, 18 H, $(CH_2)_9$), 0.87 (t, 3 H, CH_3); cmc = 1.4×10^{-4} M (H_2O); FAB high resolution mass spectrum (HRMS), calcd for $C_{32}H_{44}OP$ (cation of **1a**) 475.3130, found 475.3130. Anal. Calcd for $C_{32}H_{44}BrOP$: C, 69.18; H, 7.98. Found: C, 69.26; H, 8.00.

Diphenyl(2-hydroxyethyl)dodecylphosphonium Bromide (1b). Reaction[14] of Ph_2PCl (Aldrich) with the Grignard of n-$C_{12}H_{25}Br$ in THF gave (95%) crude n-$C_{12}H_{25}PPh_2$ as an oil which was used for preparation of **1b**. A 200-mg portion was chromatographed on a 1.1 × 30 cm column of silica gel packed in hexane with 100 mL of hexane and 250 mL of 1:9 (v/v) EtOAc–hexane. The phosphine eluted with the latter as an oil: ^1H NMR δ 7.28–7.46 (m, 10 H, Ar H), 2.03 (m, 2 H, CH_2P), 1.28–1.41 (m, 20 H, $(CH_2)_{10}$), 0.87 (t, 3 H, CH_3); EI HRMS, calcd for $C_{24}H_{35}P$ 354.2557, found 354.2467.

With the procedure for **1a**, the reaction of 4.40 g (12.5 mmol) of the above phosphine and 2.50 g (20.0 mmol) of $BrCH_2CH_2OH$ in 10 mL of $MeNO_2$ gave 4.50 g of crude material and 3.75 g (63%) of **1b** as a viscous oil after one column chromatography: ^1H NMR δ 7.64–7.86 (m, 10 H, Ar H), 5.28 (br s, 1 H, OH), 3.91 (d of t, $J_{P,H}$ = 22.0 Hz, $J_{H,H}$ = 5.7 Hz, 2 H, CH_2O), 3.43 (d of t, $J_{P,H}$ = 11.7 Hz, $J_{H,H}$ = 5.7 Hz, 2 H, PCH_2CH_2O), 3.12 (m, 2 H, CH_2P), 1.48 (m, 4 H, $CH_2CH_2CH_2P$), 1.23 (m, 16 H, $(CH_2)_8$), 0.87 (t, 3 H, CH_3); cmc = 4.0×10^{-4} M (H_2O); FAB HRMS, calcd for $C_{26}H_{40}OP$ (cation of **1b**) 399.2817, found 399.2828. Anal. Calcd for $C_{26}H_{40}BrOP$: C, 65.13; H, 8.41. Found: C, 64.98; H, 8.40.

(4-Dodecylphenyl)diphenylpropylphosphonium Bromide (2a). A mixture of 1.32 g (3.07 mmol) of 4-n-$C_{12}H_{25}C_6H_4PPh_2$[13] and 1.13 g (9.19 mmol) of n-PrBr in 5 mL of $MeNO_2$ was degassed (N_2) for 5 min, held at 80 °C for 4 h, and rotary evaporated. The residue was chromatographed on a 1.8 × 30 cm column of silica gel packed in $CHCl_3$ with 100 mL each of $CHCl_3$, 1:9 (v/v) Et_2O–$CHCl_3$, and 1:1 (v/v) Et_2O–$CHCl_3$ and 200 mL of 1:19 (v/v) MeOH–$CHCl_3$. The surfactant was eluted with the last solution to give 1.02 g (60%) of **2a** as a viscous oil: ^1H NMR δ 7.50–7.90 (m, 14 H, Ar H), 3.68 (br m, 2 H, CH_2P), 2.68 (t, J = 7.6 Hz, 2 H, CH_2Ar), 1.61 (br m, 4 H, CH_2CH_2Ar and $PCH_2CH_2CH_3$), 1.25 (m, 21 H, $(CH_2)_9$ and CH_3), 0.87 (t, 3 H, CH_3). Anal. Calcd for $C_{33}H_{46}BrP \cdot 0.5H_2O$: C, 70.45; H, 8.42. Found: C, 70.66, 70.63; H, 8.51, 8.47.

Dodecyldiphenylpropylphosphonium Bromide (2b). With the procedure for **2a**, 2.47 g (7.06 mmol) of n-$C_{12}H_{25}PPh_2$ and 2.60 g (21.2 mmol) of n-PrBr in 10 mL of $MeNO_2$ gave after chromatography 1.92 g (57%) of **2b** as a viscous oil: ^1H NMR δ 7.69–7.95 (m, 10 H, Ar H), 3.30 (m, 4 H, CH_2PCH_2), 1.49 (m, 6 H, $CH_2CH_2CH_2PCH_2CH_2$), 1.25 (m, 19 H, $(CH_2)_8$ and CH_3), 0.87 (t, 3 H, CH_3). Anal. Calcd for $C_{27}H_{42}BrP \cdot 0.5H_2O$: C, 66.66; H, 8.91. Found: C, 66.90, 66.80; H, 8.97, 8.99.

(4-Dodecylphenyl)diphenylvinylphosphonium Bromide (3a). By a literature procedure,[15] 4-n-$C_{12}H_{25}C_6H_4Ph_2P^+$-$CH_2CH_2Cl,Br^-/Cl^-$ was prepared from **1a** and was converted without purification to **3b**. Crude material (2.4 g) was chromatographed on a 3.0 × 45 cm column of silica gel packed in $CHCl_3$ with 250 mL of $CHCl_3$ and 500 mL of 1:19 (v/v) MeOH–$CHCl_3$. The surfactant eluted with the latter as a dark brown oil, and a $CHCl_3$ solution was treated with Norit (5 times; total loss of 45%) to give **3a** as a light brown oil. Rechromatography as above gave 0.81 g of **3a** as a light yellow, viscous oil: ^1H NMR δ 8.20 (d of d of d, $J_{P,H}$ = 24.9 Hz, $J_{H,H\text{-}cis}$ = 12.5 Hz, $J_{H,H\text{-}trans}$ = 18.0 Hz, 1 H, PCH), 7.47–7.90 (m, 14 H, Ar H), 7.19 (d of d, $J_{P,H}$ = 49.8 Hz, $J_{H,H\text{-}cis}$ = 12.5 Hz, 1 H, $PCH{=}CH_{cis}H_{trans}$), 6.16 (d of d, $J_{P,H}$ = 25.3 Hz, $J_{H,H\text{-}trans}$ = 18.0 Hz, 1 H, $PCH{=}CH_{cis}H_{trans}$), 2.73 (t, J = 7.0 Hz, 2 H, CH_2Ar), 1.65 (br m, 2 H, CH_2CH_2Ar), 1.25 (m, 18 H, $(CH_2)_9$), 0.87 (t, 3 H, CH_3); FAB HRMS, calcd for $C_{32}H_{42}P$ (cation of **3a**) 457.3024, found 457.3054. Anal. Calcd for $C_{32}H_{42}BrP \cdot H_2O$: C, 69.18; H, 7.98. Found: C, 69.35, 69.40; H, 7.99, 8.02.

Dodecyldiphenylvinylphosphonium Bromide (3b). From **1b**, n-$C_{12}H_{25}Ph_2P^+CH_2CH_2Cl,Br^-/Cl^-$ was prepared and converted[15] without purification to **3b**. Crude material was purified as for **3a** to give (50%) **3b** as a light yellow, viscous oil: ^1H NMR δ 7.68–7.89 (m, 10 H, Ar H), 7.53 (d of d of d, $J_{P,H}$ = 24.2 Hz, $J_{H,H\text{-}cis}$ = 12.5 Hz, $J_{H,H\text{-}trans}$ = 18.3 Hz, 1 H, PCH), 6.91 (d of d, $J_{P,H}$ = 48.0 Hz, $J_{H,H\text{-}cis}$ = 12.8 Hz, 1 H, $PCH{=}CH_{cis}H_{trans}$), 6.21 (d of d, $J_{P,H}$ = 24.2 Hz, $J_{H,H\text{-}trans}$ = 18.3 Hz, 1 H, $PCH{=}CH_{cis}H_{trans}$), 3.34 (m, 2 H, CH_2P), 1.63 (m, 4 H, $CH_2CH_2CH_2P$), 1.23 (m, 16 H, $(CH_2)_8$), 0.87 (t, 3 H, CH_3); FAB HRMS, calcd for $C_{26}H_{38}P$ (cation of **3b**) 381.2711, found: 381.2706. Anal. Calcd for $C_{26}H_{38}BrP$: C, 67.67; H, 8.30. Found: C, 67.79, 67.53; H, 8.34, 8.33.

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Registry No. **1a**, 98482-63-4; **1b**, 98482-66-7; **2a**, 98482-64-5; **2b**, 98482-67-8; **3a**, 98482-65-6; **3b**, 98482-68-9; 4-n-$C_{12}H_{25}C_6H_4PPh_2$, 65717-71-7; $BrCH_2CH_2OH$, 540-51-2; n-$C_{12}H_{25}PPh_2$, 38854-58-9; n-PrBr, 106-94-5; p-$NO_2C_6H_4OPO(OPh)_2$, 10359-36-1.

Supplementary Material Available: ^1H NMR data for **7** and $RPh_2P^+CH_2CH_2Cl,Br^-/Cl^-$ (R = 4-n-$C_{12}H_{25}C_6H_4$ and n-$C_{12}H_{25}$) and IR data for **1**, **2**, **3**, and n-$C_{12}H_{25}PPh_2$ (1 page). Ordering information is given on any current masthead page.

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