9412, 7619, 5827, 34287); ^{1}H NMR ($CDCl_3$) δ 11.66 (s, 1 H, CHO), 9.55, 9.33, 8.68 (all s, 3 H, meso H), 4.75 (m, 1 H, 2-H), 4.12 (q, 2 H, CH_2 of ester), 3.70 (m, 12 H, CH_2 of peripheral ethyl), 2.67 (m, 4 H, CH_2 of 1,2-ethyl), 1.70 (t, 21 H, CH_3 of peripheral ethyl), 1.13 (t, 3 H CH_3 of ester), -0.46 (t, 3 H, CH_3 of 3-ethyl); mass spectrum, m/e (relative intensity) 664 (M^+, 12), 604 (11), 563 (41), 548 (100). Anal. Calcd for $C_{41}H_{52}N_4O_4 \cdot H_2O$: C, 72.14; H, 7.92. Found: C, 71.86; H, 8.01.

Hydrogenation of Purpurin 11. Palladium on charcoal (10%) (20 mg) was added to a stirred solution of purpurin 11 (100 mg) in tetrahydrofuran (20 mL) containing triethylamine (2 drops) and the resulting mixture hydrogenated at room temperature, under a slight positive pressure. After 5 h, the reaction mixture was filtered and the clear solution obtained vigorously stirred in air for 2.5 h. After complete oxidation of the intermediate porphyrinogen, indicated by a brown-colored solution and followed by measuring the intensity of an absorption at 660 nm in the visible spectrum of the solution, the solvent was removed in vacuo and the residue chromatographed on silica with 1% methanol in dichloromethane for elution. The major blue band was collected, the solvent removed, and the crude product crystallized from dichloromethane–methanol to give brown microprisms of **12**. (72 mg, 72% yield): mp 142–145 °C; vis λ_{max} 403, 500, 535, 558, 610, 660 nm (ϵ 114650, 23532, 5662, 4246, 8493, 39455); ^{1}H NMR ($CDCl_3$) δ 9.55, 8.68 (both s, 2:1, 3 H, meso H) 5.08–4.87 (m, 3 H, isocyclic CH_2, H), 4.70 (t, 1 H, 2-H), 4.45 (t, 2 H, CH_2 of ester), 3.80 (t, 12 H, CH_2 of peripheral ethyl), 2.90, 2.84 (m, 4 H, 1,2-ethyl), 1.74 (m, 21 H, CH_3 of peripheral ethyl), 1.54 (t, 3 H, CH_3 of ester), -0.23 (t, 3 H, CH_3 of 3-ethyl), -1.42, -2.02 (both s, 2 H, NH); mass spectrum, m/e 634 (M^+). Anal. Calcd for $C_{41}H_{54}N_4O_2 \cdot 2H_2O$: C, 73.43; H, 8.66. Found: C, 73.26; H, 8.66.

Zinc Complex. The zinc complex was prepared as described for the zinc complex of **11** in 92% yield: vis λ_{max} 408, 515, 545, 590, 633 nm (ϵ 145474, 9858, 5377, 15832, 59444).

Nickel Complex. The nickel complex was prepared in a similar manner in 86% yield: vis λ_{max} 405, 498, 533, 588, 630 nm (ϵ 145779, 11034, 8693, 19392, 64146).

Cyclization of *meso*-[β-(Ethoxycarbonyl)vinyl]octaethylporphyrin in Air to 14. *meso*-[β-(Ethoxycarbonyl)-vinyl]octaethylporphyrin (**10**) (100 mg) in glacial acetic acid (20 mL) was heated under reflux for 24 h. The solution was cooled, the solvent removed in vacuo, and the residue chromatographed on silica with dichloromethane for elution. The first major green band was collected, the solvent removed, and the crude product crystallized from dichloromethane–methanol to give deep purple microprisms of **14** (40 mg, 40% yield): mp 145–147 °C; vis λ_{max} 438, 510, 540, 583, 653, 715 nm (ϵ 104158, 9450, 11130, 15540, 9020, 42629); ^{1}H NMR ($CDCl_3$) δ 9.47, 9.40, 9.00 (all s, 3 H meso H), 9.30 (s, 1 H, H of isocyclic ring), 7.23 (q, 1 H), 4.56 (q, 2 H, CH_2 ester), 3.83 (m, 12 H, CH_2 of peripheral ethyl), 2.50 (d, 2 H, J = 8 Hz, CH=CH_3). 2.32 (m, 2 H, CH_2 of 3-ethyl), 1.62 (m, 21 H, CH_3 of peripheral ethyl), 0.215 (t, 3 H, CH_3 of 3-ethyl), -0.23, -0.69 (both s, 2 H, NH); mass spectrum, m/e (relative intensity) 630 (M^+ 100), 601 (79), 534 (43).

Zinc Complex. The zinc complex was prepared by the usual method in 95% yield: vis λ_{max} 430, 543, 593, 630, 680 nm (ϵ 141532, 6797, 8396, 14393, 41180).

A second major green band was also collected, the solvent removed, and the residue crystallized from dichloromethane–methanol to give purple microcrystals of purpurin **11** (39 mg, 39% yield), identical with an authentic sample.

Hydrogenation of 14. Purpurin **14** (100 mg) was hydrogenated under conditions similar to those described above to yield, after workup and chromatographic purification, chlorin **12** (65 mg, 65% yield), identical with an authentic sample.

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Registry No. **8**, 52518-61-3; **9**, 99128-87-7; **10**, 61354-68-5; **11**, 99128-91-3; **11** (Zn complex), 99128-88-8; **12**, 99128-93-5; **12** (Zn complex), 99128-89-9; **12** (Ni complex), 99128-90-2; **13**, 99147-86-1; **14**, 99128-92-4; **14** (Zn complex), 99147-85-0; ethoxycarbonyl methylenetriphenylphosphorane, 1099-45-2.

Micellar Effects on Competitive Hydrolysis and Hydration of Vinylphosphonium Salts

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Vinyl phosphonium salts undergo reactions with $^-$OH in H_2O at C and P to give products of hydration and hydrolysis, respectively.[1] In a study[2] of phosphate ester hydrolysis under basic conditions catalyzed by micellar **2b**, we noted that **1b** displayed unusual C vs. P reactivity. Herein, we report a study of micellar effects on this competition with **1a–c**.[3]

At 25 °C, **1a** in ≤1.5 M NaOH yielded only **2a** from attack at C and in ≥2.0 M NaOH yielded a minor amount of **2a** (14%) and a mixture of products including **3a** (10%), **4a** (16%), **5a** (27%), and **6a** (17%) from attack at P (Chart I).[4] Thus, the regiochemistry depends on [$^-$OH]. In contrast, micellar **1b** displayed a distinctly different reactivity pattern. Predominant attack occurred at P in [$^-$OH]'s as low as 0.01 M but at C in [$^-$OH]'s ≤ 0.001 M. The former gave a complex mixture containing **3–6** and the latter **2b**. The behavior of **1c** paralleled that of **1a**, so the dependence of **1b**'s reactivity on [$^-$OH] manifests a micellar rather than a simple substituent effect.

These micellar effects represent a vivid example of the ability of cationic micelles to concentrate anionic reagents relative to the aqueous pseudophase.[6] Indeed, [$^-$OH] = 1–2 M is estimated[7] for the Stern layer of micellar **1b** in 0.01 M NaOH. For bimolecular reactions, the usual consequences of such concentration are catalysis or inhibition.[6] The results with **1b** represent a rare example of *regiochemical* consequences.[8] Indeed, there are only a few other reports[9] of such regio/chemoselectivity control.

(1) For examples, see: (a) Shutt, J. R.; Trippett, S. *J. Chem. Soc. C* **1969**, 2038. (b) Brophy, J. J.; Gallagher, M. J. *J. Chem. Soc., Chem. Commun.* **1967**, 344.

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(3) In some of the runs described below, $^-$OD–D_2O instead of $^-$OH–H_2O was actually used (see Experimental Section).

(4) (a) Shutt and Trippett[1a] reported that **1a** gives **3a**, **5a**, Ph_3PO, and Ph_3P (but not **4a** and **6a**) in aqueous 2 M NaOH at reflux. It was proposed that **3a** is formed by a rearrangement of **1a**, and **5a** via the addition of Ph_2PO^- to **1a**. In the present study, **5a** may result directly from the addition of Ph_2PO^- to **4a**, which is probably formed by a typical quaternary phosphonium salt hydrolysis:[5a] R_4P^+ $^-$OH → R_3PO + RH. (b) Hands and Mercer reported[5b] that $Ph_3P^+CH_2CH_2OH$ I^- gives (84%) **6a** in aqueous KOH at ca. 100 °C. In this study, however, only a minor amount of **6a** came from **2a** (see Experimental Section); presumably, the majority derived from **4a**. Thus, the 14% of **2a** fairly represents the maximum amount of initial $^-$OH attack at C.

(5) (a) Hudson, R. F. "Structure and Mechanism in Organo-Phosphorus Chemistry"; Academic Press: New York, 1965; pp 206–210. (b) Hands, A. R.; Mercer, A. J. H. *J. Chem. Soc.* **1965**, 6055.

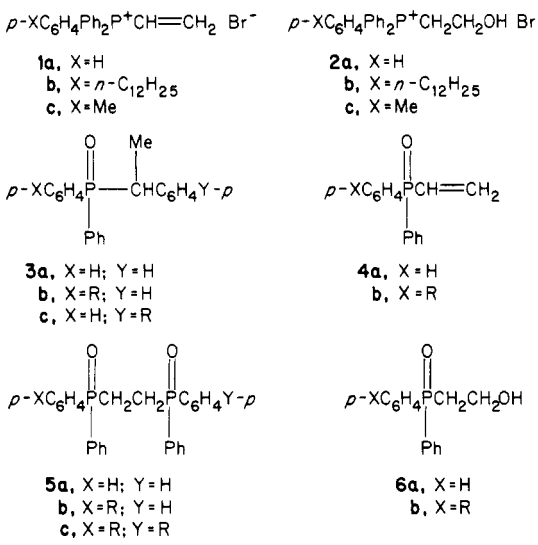
(6) Bunton, C. A. *Catal. Rev.—Sci. Eng.* **1979**, *20*, 1 and references therein.

(7) Bunton, C. A.; Hong, Y. S.; Romsted, L. S. In "Solution Behavior of Surfactants"; Mittal, K. L., Fendler, E. J., Eds.; Plenum Press: New York, 1982; Vol. 2, p 1137. An adaptation of eq 7 was used. Several calculations were made for [**1b**] = 0.001 M with K_{OH}^{Br} values of 12–21 (those given for hexadecyltrimethylammonium bromide) and β values of 0.6–0.9. It was also assumed that the density of micellar **1b** is 1 and that the Stern layer constitutes half of its volume. The CMC assumed for **1b** was that determined for **2b**.[2]

(8) Micellar catalysis would also be expected, but reaction kinetics were not studied.

0022-3263/86/1951-1350$01.50/0

Chart I[a]



[a] R = n-$C_{12}H_{25}$ or Me.

Regioselectivity effects were found in micellar reactions of $^-$OH with *N*-alkyl-4-cyanopyridinium ions,[9a,b] and chemoselectivity effects in micellar dediazoniations.[9c,d] In these and the present study it is possible that medium effects also contributed to the observed selectivities since the Stern layer of an ionic micelle typically has a dielectric constant less than that of H_2O and about that of EtOH/MeOH.[10]

Overall, concentration of $^-$OH by the Stern layer of micellar **1b** in 0.01 M NaOH resulted in regioselectivity that was obtained only at much higher [$^-$OH]'s with nonmicellar analogues.

Experimental Section

General Procedures. ^{1}H NMR spectra were recorded at 270 MHz with Me_4Si and $Me_3Si(CD_2)_2CO_2Na$ as internal standards in $CDCl_3$ and D_2O, respectively. Electron-impact high-resolution mass spectra (HRMS) were obtained at 70 eV on a VG-ZAB 1F spectrometer. Elemental analyses were performed by Atlantic Microlab, Atlanta, GA. Recrystallizations were at 25 °C.

Solvents and Materials. D_2O (Aldrich, 99.8% D) and 20 wt % DCl–D_2O (Aldrich, >99% D) were used as received. **1a** (Aldrich) was recrystallized from 2:1 (v/v) *t*-BuOH–Et_2O, mp 180–181 °C. **1b**[2] (oil), **2a**,[11] mp 219–220 °C, and **2b**,[2] mp 84–87 °C (precipitated from $MeNO_2$ by Et_2O), were prepared by the literature procedures. The critical micelle concentration of **2b** is 1.4×10^{-4} M (H_2O),[2] and that of **1b** should be similar.

***p*-Tolyldiphenylvinylphosphonium Bromide (1c).** By a literature procedure,[12] p-$MeC_6H_4Ph_2P^+CH_2CH_2Cl$ Br^-/Cl^- was prepared (99%) from **2c**: ^{1}H NMR ($CDCl_3$) δ 7.52–7.89 (m, 14 H, Ar H), 4.42 (d of t, $J_{P,H}$ = 11.7 Hz, $J_{H,H}$ = 6.2 Hz, 2 H, CH_2P), 4.02 (d of t, $J_{P,H}$ = 20.5 Hz, $J_{H,H}$ = 6.2 Hz, 2 H, CH_2Cl), 2.50 (s, 3 H, CH_3). This crude material was converted[12] into **1c** and the product recrystallized twice from 10:1 EtOAc–CH_2Cl_2 to give (46%) of **1c**: mp 143–145 °C; ^{1}H NMR ($CDCl_3$) δ 8.18 (d of d of d, $J_{P,H}$ = 24.9 Hz, $J_{H,H-cis}$ = 12.5 Hz, $J_{H,H-trans}$ = 18.0 Hz, 1 H, PCH), 7.53–7.87 (m, 14 H, Ar H), 7.18 (d of d, $J_{P,H}$ = 49.8 Hz, $J_{H,H-cis}$ = 12.5 Hz, 1 H, PCH=$CH_{cis}H_{trans}$), 6.16 (d of d, $J_{P,H}$ = 25.3 Hz, $J_{H,H-trans}$ = 18.0 Hz, 1 H, PCH=$CH_{cis}H_{trans}$), 2.51 (s, 3 H, CH_3). Anal. Calcd for $C_{21}H_{20}BrP \cdot 0.5H_2O$: C, 64.29; H, 5.39. Found: C, 64.26, 64.23; H, 5.43, 5.45.

***p*-Tolyldiphenyl(2-hydroxyethyl)phosphonium Bromide (2c).** A mixture of 11.1 g (40.0 mmol) of p-$MeC_6H_4PPh_2$ (Alfa) and 10.0 g (80.0 mmol) of $BrCH_2CH_2OH$ (Aldrich) was held at 100 °C for 1 h under N_2. Volatiles were removed at 80 °C (0.05 mmHg), and recrystallization of the residue from 8:1 EtOAc–EtOH gave 11.5 g (72%) of **2c**: mp 146–147 °C; ^{1}H NMR ($CDCl_3$) δ 7.46–7.80 (m, 14 H, Ar H), 4.65 (br s, 1 H, OH), 4.06 (d of t, $J_{P,H}$ = 17.6 Hz, $J_{H,H}$ = 6.2 Hz, 2 H, CH_2O), 3.75 (d of t, $J_{P,H}$ = 11.7 Hz, $J_{H,H}$ = 6.2 Hz, 2 H, CH_2P), 2.48 (s, 3 H, CH_3). Anal. Calcd for $C_{21}H_{22}BrOP$: C, 62.86; H, 5.53. Found: C, 62.89; H, 5.56.

(Oxydiethylene)bis[triphenylphosphonium] Dibromide (7). A solution of 0.74 g (2.0 mmol) of **1a** in 50 mL of H_2O was added during ca. 10 s to a solution of 0.78 g (2.0 mmol) of **2a** in 50 mL of 0.2 M NaOH at 25 °C under N_2. After 1 min, the reaction mixture was acidified with 3.0 mL of concentrated hydrobromic acid and extracted with three 50-mL portions of $CHCl_3$. The combined extracts were dried (Na_2SO_4) and rotary evaporated to give 1.45 g of crude material that was column chromatographed on silica gel packed in $CHCl_3$ with MeOH–$CHCl_3$ elution. **7** (430 mg) eluted with 10% MeOH–$CHCl_3$, and recrystallization from 10:1 EtOAc–CH_2Cl_2 gave 250 mg (21%) of **7**: mp 248–249.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.74–7.78 (m, 30 H, Ar H), 3.90 (br m, 8 H, CH_2CH_2). Anal. Calcd for $C_{40}H_{38}Br_2OP_2 \cdot H_2O$: C, 62.03; H, 5.21. Found: C, 61.91, 61.84; H, 5.10, 5.12.

Reactions of 1a in Aqueous Base. To 0.25 mL of 0.02 M **1a** in D_2O at 25 °C was added 0.25 mL of 0.20 M NaOD–D_2O. After a given time at 25 °C, the solution was acidified with 1 drop of 20 wt % DCl–D_2O and analyzed by ^{1}H NMR. With a 30-min reaction time, the product mixture contained 83% $Ph_3P^+CD_2CH_2OD$ Br^-/Cl^- (**2a**-*d*), 10% $(Ph_3P^+CD_2CH_2)_2O$ $2Br^-/Cl^-$ (**7**-*d*), and 7% $Ph_3P^+CD{=}CH_2$ Br^-/Cl^- (**1a**-*d*). With reaction times of 2–24 h, only **2a**-*d* was detected.

By the above procedure, reaction mixtures were prepared at 25 °C by the addition of 0.25 mL of 0.02 M **1a** in D_2O to each of 0.25 mL of 1.0, 2.0, 3.0, 4.0, and 5.0 M NaOD–D_2O. After 10 min at 25 °C, each solution was acidified with 5 drops of 20 wt % DCl–D_2O and analyzed by ^{1}H NMR. The first three solutions remained clear, and only **2a**-*d* was detected. The last two solutions became turbid several seconds after preparation and contained a complex mixture including benzene and **2a**-*d*. Analogous runs with **1c** gave similar results.

Under N_2, a reaction mixture prepared by the addition of 200 mL of 5.0 M NaOH to a solution of 1.47 g (4.00 mmol) of **1a** in 200 mL of H_2O was stirred at 25 °C for 30 min and cooled to 5 °C. After the addition of 120 mL of concentrated hydrochloric acid and 80 g of NaCl, the reaction mixture was extracted with three 100-mL portions of $CHCl_3$. The combined extracts were dried (Na_2SO_4) and rotary evaporated, and the crude product was chromatographed on basic alumina (Fisher, Brockman Activity 1) packed in Et_2O with Et_2O–MeOH elution. **3a** (117 mg, 10%) eluted with 1% MeOH–Et_2O and was recrystallized from cyclohexane: mp 156–158 °C (lit.[1a] mp 140–141 °C); ^{1}H NMR ($CDCl_3$) δ 7.17–7.94 (m, 15 H, Ar H), 3.60 (d of q, $J_{P,H}$ = 8.1 Hz, $J_{H,H}$ = 7.3 Hz, 1 H, CH), 1.58 (d of d, $J_{P,H}$ = 16.1 Hz, $J_{H,H}$ = 7.3 Hz, 3 H, CH_3); HRMS, calcd for $C_{20}H_{19}OP$ 306.1173, found 306.1167. **4a** (145 mg, 16%) eluted with 2% MeOH–Et_2O and was recrystallized from 5:1 hexane–EtOAc: mp 114–115 °C (lit.[1a] mp 114–115 °C). **5a** (232 mg, 27%) eluted with 3% MeOH–Et_2O and was recrystallized from 5:1 EtOAc–CH_2Cl_2: mp 264–266 °C (lit.[1a] mp 268–270 °C). **6a** (168 mg, 17%) eluted with 10% MeOH–Et_2O and was recrystallized from 2:1 hexane–EtOAc: mp 92–93 °C (lit.[5b] mp 94.5–95.5 °C). $Ph_3P^+CH_2CH_2OH$ Cl^- (196 mg, 14%) eluted with 50% MeOH–Et_2O and was recrystallized from EtOH: mp 234–236 °C (lit.[13] mp 233 °C).

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Reactions of 1b in Aqueous Base. To 0.25 mL of 0.02 M **1b** in D_2O was added 0.25 mL of pH 11[14] 0.10 M carbonate buffer in D_2O. After 25 min at 25 °C, only *p*-*n*-$C_{12}H_{25}C_6H_4Ph_2P^+CD_2CH_2OD$ Br^- (**2b**-*d*) and/or (*p*-*n*-$C_{12}H_{25}C_6H_4Ph_2P^+CD_2CH_2)_2O$ $2Br^-$ were detected by ^1H NMR. The same result was obtained with the substitution of pH 10 0.10 M carbonate buffer in D_2O. With extended reaction times, conversion to **6a**/**6b** is likely, analogous to that of **1a** to **6a**.[4b,5b]

A reaction mixture was prepared from 1.0 mL of 0.02 M NaOD-D_2O and 1.0 mL of 0.002 M **1b** in D_2O. After 3 min at 25 °C, an oil had precipitated, and the reaction mixture was acidified with 20 wt % DCl-D_2O. By ^1H NMR, no organic material was detected in the supernatant solution. The oil was washed with H_2O and dried under vacuum; its ^1H NMR spectrum ($CDCl_3$) was similar to that of the crude product obtained from **1b** in 0.1 M NaOH.

As above for **1a**, 0.27 g (0.50 mmol) of **1b** in 25 mL of H_2O was treated with 25 mL of 0.2 M NaOH. The 0.20 g of crude product was chromatographed on basic alumina packed in Et_2O with MeOH-Et_2O elution. **4b** and **3b**/**3c** (7:1 mol ratio, 91 mg, 45%) eluted together with 1% MeOH-Et_2O. **4a**[1a] (13 mg, 11%) eluted with 1% MeOH-Et_2O. **5b** (trace) and **5c** (21 mg, 11%) eluted with 3% MeOH-Et_2O. **6a** (trace), **6b**, and *p*-*n*-$C_{12}H_{25}C_6H_4Ph_2P^+CH_2CH_2OH$ Cl^-/Br^- (2:1, 22 mg, 10%) eluted with 10-50% MeOH-Et_2O. **5a** was not detected. New compounds were identified by ^1H NMR in comparison with analogues from **1a** and by HRMS. **3b**/**3c**: calcd for $C_{32}H_{43}OP$ 474.3051, found, 474.3032. **4b**: calcd for $C_{26}H_{37}OP$ 396.2581, found 396.2551. **5b**: calcd for $C_{38}H_{48}O_2P_2$ 598.3128, found 598.3083. **5c**: calcd for $C_{50}H_{72}O_2P_2$ 766.5007, found 766.4990. **6a**: calcd for $C_{14}H_{15}O_2P$ 246.0810, found 246.0818. **6b**: calcd for $C_{26}H_{39}O_2P$ 414.2688, found 414.2686.

Stability of 2a in Aqueous Base. To 0.25 mL of 0.02 M **1a** was added 0.25 mL of 5.0 M NaOD-D_2O. After 30 min at 25 °C, the solution was acidified with 20 wt % DCl-D_2O. By ^1H NMR it contained ca. 10% $Ph_2P(O)CD_2CH_2OD$ (**6a**-*d*), with the remainder being **2a**-*d*.

Reaction of 1c in Aqueous Base. As for **1a**, 0.77 g (2.0 mmol) of **1c** in 100 mL of H_2O was treated with 100 mL of 5.0 M NaOH. The 0.80 g of crude product was chromatographed on basic alumina packed in Et_2O with MeOH-Et_2O elution. **3b** and **3c** (1:1 mol ratio, 93 mg, 14%) eluted with 1% MeOH-Et_2O. **4a**[1a] (trace) and **4b** (132 mg, 27%) eluted with 2% MeOH-Et_2O. **5b** (trace) and **5c** (144 mg, 31%) eluted with 3% MeOH-Et_2O. **6a**[5b] (trace) and **6b** (16 mg, 3%) eluted with 10% MeOH-Et_2O. *p*-$MeC_6H_4Ph_2P^+CH_2CH_2OH$ Cl^-/Br^- (52 mg, 7%) eluted with 50% MeOH-Et_2O. **5a** was not detected. New compounds were identified by ^1H NMR in comparison with analogues from **1a** and by HRMS. **3b**/**3c**: calcd for $C_{21}H_{21}OP$ 320.1330, found 320.1315. **4b**: calcd for $C_{15}H_{15}OP$ 242.0860, found 242.0844. **5b**: calcd for $C_{27}H_{26}O_2P_2$ 444.1407, found 444.1395. **5c**: calcd for $C_{28}H_{28}O_2P_2$ 458.1564, found 458.1554. **6b**: calcd for $C_{15}H_{17}O_2P$ 260.0966, found 260.0986.

Acknowledgment is gratefully made to the U.S. Army Research Office and the Marathon Oil Company.

Registry No. **1a**, 5044-52-0; **1a**-*d*, 7237-37-8; **1b**, 98482-65-6; **1c**, 100449-69-2; **2a**, 7237-34-5; **2a**-*d*, 100449-72-7; **2b**-*d*, 100466-22-6; **2c**, 100449-71-6; **3a**, 23896-93-7; **3b**, 100449-76-1; **3c**, 100449-77-2; **4a**, 2096-78-8; **4b**, 100449-75-0; **5a**, 4141-50-8; **5b**, 100449-78-3; **5c**, 100466-23-7; **6a**, 887-21-8; **6a**-*d*, 100449-80-7; **6b**, 100466-24-8; **7**, 5368-62-7; **7**-*d*, 100449-73-8; *p*-$MeC_6H_4Ph_2P^+CH_2CH_2Cl,Br^-$, 100449-70-5; *p*-$MeC_6H_4Ph_2P^+CH_2CH_2Cl,Cl^-$, 100449-82-9; *p*-$MeC_6H_4PPh_2$, 1031-93-2; $BrCH_2CH_2OH$, 540-51-2; $Ph_3P^+CH_2CH_2OH,Cl^-$, 23250-03-5; $(Ph_3P^+CD_2CH_2)_2O,2Cl^-$, 100449-83-0; $Ph_3P^+CD{=}CH_2,Cl^-$, 100449-84-1; $Ph_3P^+CD_2CH_2OD,Cl^-$, 100449-85-2; $(p\text{-}n\text{-}C_{12}H_{25}C_6H_4Ph_2P^+CD_2CH_2)_2O,2Br^-$, 100449-74-9; *p*-*n*-$C_{12}H_{25}C_6H_4Ph_2P^+CH_2CH_2OH,Cl^-$, 100449-79-4; *p*-$MeC_6H_4Ph_2P^+CH_2CH_2OH,Cl^-$, 100449-81-8.

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(14) This and the pH 10 value below were calculated for the corresponding protio systems.

Ester Cleavage by a Phenolic Quaternary Phosphonium Surfactant

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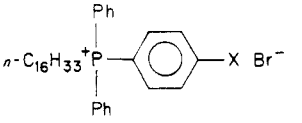
Numerous functionalized surfactants have been used to catalyze the hydrolysis of carbon and phosphorus esters.[1] Most of these have been quaternary ammonium systems. Previously, we described[2] the first functionalized quaternary phosphonium surfactants, and herein we report the synthesis and application of additional examples **1**-**3**.



1, X = OH
1a, X = O⁻
2, X = OCOMe
3, X = OMe

Reaction of *p*-$MeOC_6H_4PPh_2$ with *n*-$C_{16}H_{33}Br$ gave **3**, which was converted to **1** with hydrobromic acid. Acetylation of **1** with MeCOCl yielded **2**. By UV and ^{31}P NMR methods, micellar **1** has a pK_a of 6.6. Thus, the *p*-$C_{16}H_{33}Ph_2{}^+P$ substituent and micellization[3] combine to give an acidity enhancement of ca. 3 pK_a units relative to phenol (9.86).[4]

Phenolic **1** in comicellar form with hexadecyltrimethylammonium bromide (HTABr) was used as a catalyst for hydrolyses of *p*-nitrophenyl acetate (**4**) and sodium 4-acetoxy-3-nitrobenzenesulfonate (**5**), and the results are summarized in Tables I and II. **1**'s solubility characteristics precluded its use alone.

In pH 9 buffer with [**1**] = [HTABr] = 0.001 M, the pseudo-first-order rate constant (k_ψ) for hydrolysis of **4** is 2.7×10^{-3} s^{-1} (entry 1). Compared to reactions with **3** substituted for **1** (entry 2), with [HTABr] = 0.002 M (entry 3), and without surfactant (entry 4), that with **1** is 2.7, 5, and 13 times faster, respectively. These facts are consistent with the involvement of **1a** in nucleophilic attack on micellar bound **4** to give **2** (eq 1), which can undergo deacylation to regenerate **1a** (eq 2). At pH 9, **1** is >99% ionized to **1a**. The reaction of eq 2 was performed independently with [**2**] = 0.0001 M and [HTABr] = 0.002 M, and k_ψ = 5.4×10^{-3} s^{-1} resulted (entry 5). Comparison of entries 1 and 5 suggests that **2** decomposes faster than it is formed under the conditions of the former, i.e., that **1** is a turnover catalyst.[5] A conclusive demonstration of **1**'s turnover capability with [**4**] > [**1**] = 0.001 M was precluded by **4**'s limited solubility. Furthermore, lower [**1**]s could not be

1a + **4**(**5**) →
2 + *p*-$NO_2C_6H_4O^-$[4-($Na^+{}^-O_3S$)-2-$NO_2C_6H_3O^-$] (1)

$$\mathbf{2} \xrightarrow[H_2O]{^-OH} \mathbf{1a} + MeCO_2^- \qquad (2)$$

(1) For a summary and examples, see: Moss, R. A.; Ihara, Y. *J. Org. Chem.* **1983**, *48*, 588 and references therein.
(2) Jaeger, D. A.; Bolikal, D. *J. Org. Chem.* **1985**, *50*, 4635.
(3) For other Nakai, and a discussion of such acidity enhancement, see: Moss, R. A.; Dix, F. M. *J. Org. Chem.* **1981**, *46*, 3029.
(4) Jencks, W. P.; Gilchrist, M. *J. Am. Chem. Soc.* **1968**, *90*, 2622.
(5) For recent examples of functionalized surfactants which perform as turnover catalysts in ester hydrolysis, see: (a) Menger, F. M.; Whitesell, L. G. *J. Am. Chem. Soc.* **1985**, *107*, 707. (b) Moss, R. A.; Alwis, K. W.; Shin, J.-S. *Ibid.* **1984**, *106*, 2651.

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