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Preparation and Characterization of Base-Sensitive Destructible Surfactants

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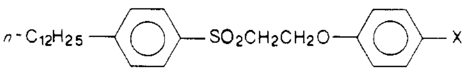
Destructible surfactants 4-*n*-$C_{12}H_{25}C_6H_4SO_2CH_2CH_2OC_6H_4X$-4 (**1**, X = N^+Me_3,NO_3^-; **2**, X = SO_3^-,K^+) were prepared, and their stability/lability characteristics in aqueous micellar solutions with respect to E1cB elimination to give 4-*n*-$C_{12}H_{25}C_6H_4SO_2CH{=}CH_2$ (**7**) and HOC_6H_4X-4 (**8**/**9**) were determined by ^1H NMR. In 0.001 and 0.1 M DCl, both **1** and **2** were stable for 24 h at 75 °C. In D_2O alone at 25 °C, **1** slowly decomposed, and **2** was stable. At 25 °C, **1** decomposed completely within 10 min in 0.1 M $NaHCO_3$, whereas **2** was more stable in 0.1 M K_2CO_3. The difference in reactivities for **1** and **2** was ascribed to a combination of electronic and micellar effects. Support for the latter was found in a comparison of **2**'s behavior with that of 4-$MeC_6H_4SO_2CH_2CH_2OC_6H_4SO_3Na$-4 (**10**).

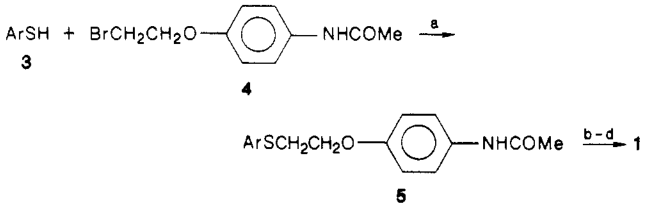
A destructible (cleavable) surfactant can be converted to nonsurfactant products under mild conditions after its use for any one of a number of purposes, thereby eliminating potentially serious emulsion or other problems in subsequent manipulations. Various examples of such surfactants with different stability/lability characteristics have been described[2] along with actual and possible applications. Herein, we report the synthesis and characterization of **1** and **2** as the first examples of a new class of destructible surfactants that are stable under acidic but labile under basic conditions.



1, X = N^+Me_3, NO_3^-
2, X = SO_3^-, K^+

Cationic **1** was prepared as outlined in Scheme I. Reaction of thiol **3** with bromide **4**, derived from $BrCH_2CH_2Br$ and 4-$MeCONHC_6H_4OH$, gave sulfide **5**. Oxidation of **5** to the corresponding sulfone followed by deprotection and permethylation of the resultant amino group gave **1**. Anionic **2** was prepared as outlined in Scheme II. Reaction of **3** with $BrCH_2CH_2OPh$ yielded sulfide **6**, and the sulfone derived from its oxidation was sulfonated followed by neutralization to give **2**.

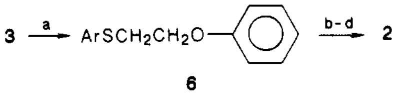
Scheme I[a]



Ar = 4-*n*-$C_{12}H_{25}C_6H_4$

[a] (a) NaOEt, EtOH; (b) H_2O_2, $MeCO_2H$; (c) HCl, H_2O, EtOH; (d) $(MeO)_2SO_2$, $NaNO_3$.

Scheme II[a]



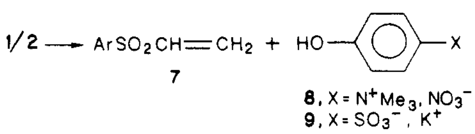
[a] (a) NaOEt, EtOH, $BrCH_2CH_2OPh$; (b) H_2O_2, $MeCO_2H$; (c) H_2SO_4; (d) KOH.

Table I. Stability/Lability Characteristics of 0.005 M 1, 2, and 10 in D_2O Solutions[a]

entry	compd	additive[b]	time, h	% dec[c]
1	1	none	6	0
			48	11
			148	33
2	1	0.1 M CD_3CO_2D	1008	0
3[d]	1	0.001 M DCl	24	0
4[d]	1	0.1 M DCl	24	0
5	1	0.1 M $NaHCO_3$	0.17	100
6	2	none	48	0
7	2	0.001 M DCl	144	0
8[d]	2	0.001 M DCl	24	0
9[d]	2	0.1 M DCl	24	0
10	2	0.01 M K_2CO_3	10	0
11	2	0.1 M K_2CO_3	2	0
			4	10
12	2	0.01 M KOD	1.2	5
			10	50
			25	100
13	10	none	48	3
14[d]	10	0.1 M DCl	24	0
15	10	0.1 M $NaHCO_3$	1	0
			24	50
			48	70
16	10	0.1 M Na_2CO_3	0.17	90

[a] At 25 °C unless noted otherwise. [b] $Me_3Si(CH_2)_3SO_3Na$ also present as internal standard. [c] Determined by ^1H NMR; see Experimental Section for composition of reaction mixtures. [d] At 75 °C.

The critical micelle concentrations (cmc's) of **1** and **2** at 25 °C in 0.01 M $MeCO_2H$ are 7.6×10^{-5} and 4.0×10^{-5} **M**, respectively. Their stability/lability characteristics with respect to base-catalyzed elimination to give vinyl sulfone **7** and phenols **8** and **9**, respectively (eq 1), are summarized in Table I. Note that both **1** and **2** were stable for extended periods in acidic media (pD 1, entries 4 and 9; pD 3, entries 3, 7, and 8) up to 75 °C. However, they displayed substantially different behavior in other media. Surfactant **1** decomposed slowly in water alone (entry 1) and completely within 10 min in 0.1 M $NaHCO_3$ (entry 5). On the other hand, surfactant **2** was stable in water (entry 6) and



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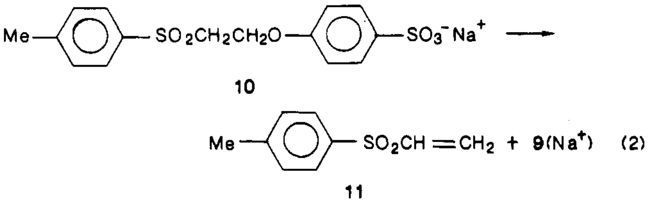
[2] (a) Jaeger, D. A.; Martin, C. A.; Golich, T. G. *J. Org. Chem.* **1984**, *49*, 4545. (b) Keana, J. F. W.; Guzikowski, A. P.; Morat, C.; Volwerk, J. J. *Ibid.* **1983**, *48*, 2661. (c) Jaeger, D. A.; Ward, M. D. *Ibid.* **1982**, *47*, 2221. (d) Jaeger, D. A.; Frey, M. R. *Ibid.* **1982**, *47*, 311. (e) Cuomo, J.; Merrifield, J. H.; Keana, J. F. W. *Ibid.* **1980**, *45*, 4216. (f) Martin, C. A.; Golich, T. G.; Jaeger, D. A. *J. Colloid Interface Sci.* **1984**, *99*, 561. (g) Epstein, W. W.; Jones, D. S.; Bruenger, E.; Rilling, H. C. *Anal. Biochem.* **1982**, *119*, 304. (h) Saji, T.; Hoshino, K.; Aoyagui, S. *J. Chem. Soc., Chem. Commun.* **1985**, 865. (i) Hayashi, Y.; Shirai, F.; Shimizu, T.; Nagano, Y.; Teramura, K. *J. Am. Oil Chem. Soc.* **1985**, *62*, 555.

0022-3263/86/1951-3956$01.50/0

even in 0.01 M K_2CO_3 (entry 10). However, it decomposed slowly in 0.1 M K_2CO_3 (entry 11) and 0.01 M KOD (entry 12).

The difference in labilities for **1** and **2** derives from two factors. The first involves the fact that $4\text{-}Me_3N^+C_6H_4O^-$ should be a better leaving group than $4\text{-}^-O_3SC_6H_4O^-$, reflecting the Hammett σ_p's[3] of 0.88 and 0.09 for N^+Me_3 and SO_3^-, respectively. The pK_a of $4\text{-}Me_3N^+C_6H_4OH$ is 8.21,[4a] and that of $4\text{-}^-O_3SC_6H_4OH$ is 8.95.[4b] The second factor involves micellar phenomena. Due to electrostatic effects, the Stern layers of aqueous cationic and anionic micelles have pH's that are greater than and less than, respectively, that of a given aqueous pseudophase.[5] Thus, for the base-catalyzed elimination of eq 1, micellar **1** will have a greater and micellar **2** a lesser reactivity than expected simply on the basis of the medium's pH. Results with **10**, a nonsurfactant analogue of **2**, are included in Table I and support the proposed micellar effect. Compound **10** decomposed rapidly in 0.1 M Na_2CO_3 to **9** and **11** (eq 2), whereas **2** was much more stable in 0.1 M K_2CO_3 (entries 16 and 11, respectively). Stirling and co-workers[6] found that substrates of the type XCH_2CH_2OPh, wherein X = $PhSO_2$ or another electron-withdrawing group, undergo E1cB elimination. Therefore, by analogy, it is likely that eq 1 and 2 follow this mechanism also.



In summary, surfactants **1** and **2**, in combination with previously reported destructible surfactants,[2] present a wide variety of stability/lability characteristics that will allow broad applications.

Experimental Section

General Procedures and Materials. ^1H (270-MHz) and ^{13}C (67.8-MHz) NMR spectra were recorded with Me_4Si as internal standard in $CDCl_3$ unless noted otherwise. Electron impact (EI) and fast atom bombardment (FAB) high-resolution mass spectra (HRMS) were obtained on a VG-ZAB 1F spectrometer and by the Midwest Center for Mass Spectrometry, a National Science Foundation Regional Instrumentation Facility. Cmc's were measured as before.[7] All preparative reactions were under N_2, and combined extracts were dried (Na_2SO_4) and rotary evaporated to leave crude product. Recrystallizations were at 25 °C unless noted otherwise. All melting points are uncorrected. Elemental analyses were performed by Atlantic Microlab, Atlanta, GA. D_2O (99.8% D, Aldrich) and $4\text{-}HOC_6H_4SO_3Na\cdot 2H_2O$ (Eastman Kodak) were used as received. $DCl\text{-}D_2O$ (20 wt %, 99+% D, Aldrich) and $KOD\text{-}D_2O$ (40 wt %, 98+% D, Aldrich) were standardized before use.

***N*-[4-(2-Bromoethoxy)phenyl]acetamide (4).** A mixture of 12.1 g (80.0 mmol) of $4\text{-}HOC_6H_4NHCOMe$ (Aldrich), 60.1 g (0.320 mol) of $BrCH_2CH_2Br$, and 11.8 g of 30% (w/w) $NaOH\text{-}H_2O$ (88.2 mmol) was refluxed for 6 h and rotary evaporated. A solution of the resultant solid in 500 mL of CH_2Cl_2 was washed with three 55-mL portions of 5% $NaOH\text{-}H_2O$, dried (Na_2SO_4), and rotary evaporated to give 17.1 g of crude **4**. This material was recrystallized from 1:1 (v/v) $H_2O\text{-}EtOH$ to yield 12.9 g (63%) of **4**: mp 125.5–126 °C; ^1H NMR δ 6.87 and 7.40 (AA′XX′, $J_{AX} + J_{AX'}$ = 9 Hz, 4 H, Ar H), 7.19 (br s, 1 H, NH) 4.27 (t, J = 6 Hz, 2 H, CH_2O), 3.62 (t, J = 6 Hz, 2 H, CH_2Br), 2.16 (s, 3 H, CH_3); IR (KBr) 3285 (m), 3250 (m), 3195 (w), 3135 (m), 3090 (m), 1655 (s), 1610 (s), 1545 (s), 1505 (s), 1407 (m), 1370 (m), 1270 (m), 1240 (s), 1174 (w), 1080 (m), 1015 (m), 820 cm^{-1} (s); EI HRMS calcd for $C_{10}H_{12}Br^{79/81}NO_2$ 257.0051 and 259.0031, found 257.0049 and 259.0023.

***N*-[4-[2-[(4-Dodecylphenyl)thio]ethoxy]phenyl]acetamide (5).** $n\text{-}C_{12}H_{25}C_6H_5$ (Aldrich) was converted to $4\text{-}n\text{-}C_{12}H_{25}C_6H_4SH$ (**3**)[8] through $4\text{-}n\text{-}C_{12}H_{25}C_6H_4SO_3K$ and $4\text{-}n\text{-}C_{12}H_{25}C_6H_4SO_2Cl$ by the literature procedure.[8] To 45 mL of 0.48 M $NaOEt\text{-}EtOH$ (21.6 mmol) was added 6.00 g (21.5 mmol) of **3**, followed by 5.56 g (21.5 mmol) of **4**. The reaction mixture was refluxed for 1 h, added to 225 mL of aqueous 10% NaCl, and extracted with three 100-mL portions of CH_2Cl_2. The combined extracts yielded crude material that was recrystallized from EtOAc to give 7.02 g (72%) of **5**: mp 117.5–118.5 °C; ^1H NMR δ 6.78–7.40 (m, 9 H, Ar H + NH), 4.09 (t, J = 7 Hz, 2 H, CH_2O), 3.22 (t, J = 7 Hz, 2 H, CH_2S), 2.57 (t, J = 7 Hz, 2 H, CH_2Ar), 2.15 (s, 3 H, CH_3CO), 1.58 (br m, 2 H, CH_2CH_2Ar), 1.25 (s, 18 H, $(CH_2)_9$), 0.88 (t, 3 H, CH_3); IR (KBr) 3325 (s), 2960 (s), 2920 (s), 2850 (s), 1665 (s), 1605 (s), 1545 (s), 1510 (s), 1492 (m), 1465 (m), 1408 (m), 1370 (m), 1319 (m), 1265 (s), 1252 (s), 1185 (m), 1172 (m), 1112 (m), 1095 (m), 1072 (m), 1015 (s), 890 (m), 822 (s), 802 (m), 780 (m), 718 cm^{-1} (m). Anal. Calcd for $C_{28}H_{41}NO_2S$: C, 73.80; H, 9.07. Found: C, 73.54; H, 9.10.

***N*-[4-[2-[(4-Dodecylphenyl)sulfonyl]ethoxy]phenyl]acetamide.** A mixture of 6.98 g (15.3 mmol) of **5**, 6.25 mL of 30% $H_2O_2\text{-}H_2O$ (61.2 mmol), and 95 mL of glacial $MeCO_2H$ was refluxed for 30 min and added to 80 mL of H_2O. The resultant mixture was extracted with three 170-mL portions of $CHCl_3$, and the combined extracts, after being washed with saturated $NaHCO_3\text{-}H_2O$ and H_2O, gave the crude product, which was recrystallized from 25 mL of 1:1 (v/v) EtOAc–hexane to yield 5.05 g (68%) of the sulfone: mp 107.5–109.5 °C; ^1H NMR δ 6.58–7.86 (m, 8 H, Ar H), 7.09 (br s, 1 H, NH), 4.32 (t, J = 6 Hz, 2 H, CH_2O), 3.56 (t, J = 6 Hz, 2 H, CH_2SO_2), 2.70 (t, J = 8 Hz, 2 H, CH_2Ar), 2.16 (s, 3 H, CH_3CO), 1.53 (br m, 2 H, CH_2CH_2Ar), 1.26 (s, 18 H, $(CH_2)_9$), 0.88 (t, 3 H, CH_3); IR (KBr) 3305 (m), 2925 (s), 2855 (s), 1658 (s), 1600 (s), 1538 (s), 1512 (s), 1472 (m), 1435 (m), 1415 (w), 1396 (w), 1343 (s), 1278 (s), 1182 (s), 1123 (m), 1066 (m), 868 (m), 850 (w), 796 (m), 714 cm^{-1} (w). Anal. Calcd for $C_{28}H_{41}NO_4S$: C, 68.95; H, 8.47. Found: C, 69.07; H, 8.51.

4-[2-[(4-Dodecylphenyl)sulfonyl]ethoxy]aniline. A general procedure was used.[9] A mixture of 3.93 g (8.06 mmol) of the above amide, 40 mL of concentrated hydrochloric acid, and 40 mL of EtOH was refluxed for 3 h, cooled to 25 °C, and filtered to collect the precipitated ammonium hydrochloride. This material was washed with EtOH (−10 °C) and added to 110 mL of 5% $NaHCO_3\text{-}H_2O$. The resultant mixture was extracted with three 50-mL portions of $CHCl_3$, and the combined extracts gave 2.73 g of the crude product, which on recrystallization at 4 °C from 40 mL of 3:1 (v/v) EtOAc–EtOH yielded 2.00 g (56%) of the title amine: mp 112.5–113 °C; ^1H NMR δ 7.35 and 7.81 (AA′XX′, $J_{AX} + J_{AX'}$ = 8 Hz, 4 H, $CH_2C_6H_4SO_2$), 6.54 (AA′BB′, 4 H, $OC_6H_4NH_2$), 4.27 (t, J = 6 Hz, 2 H, CH_2O), 3.54 (t, J = 6 Hz, 2 H, CH_2SO_2), 3.45 (br s, 2 H, NH_2), 2.69 (t, J = 8 Hz, 2 H, CH_2Ar), 1.63 (br m, 2 H, CH_2CH_2Ar), 1.26 (s, 18 H, $(CH_2)_9$), 0.88 (s, 3 H, CH_3); IR (KBr) 3435 (m), 3365 (m), 2920 (s), 2847 (s), 1630 (m), 1593 (m), 1509 (s), 1465 (m), 1386 (m), 1302 (s), 1235 (s), 1180 (m), 1137 (s), 1084 (m), 1070 (m), 1020 (w), 1010 (w), 810 (s), 718 cm^{-1} (s). Anal. Calcd for $C_{26}H_{39}NO_3S$: C, 70.07; H, 8.82. Found: C, 70.15; H, 8.93.

[4-[2-[(4-Dodecylphenyl)sulfonyl]ethoxy]phenyl]trimethylammonium Nitrate (1). A mixture of 0.50 g (1.1 mmol) of the above amine, 0.51 g (6.1 mmol) of $NaHCO_3$, 0.53 g (4.2 mmol) of $(MeO)_2SO_2$, and 6 ml of EtOH was stirred for 20 h at

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(3) McDaniel, D. H.; Brown, H. C. *J. Org. Chem.* **1958**, *23*, 420.

(4) (a) Oae, S.; Price, C. C. *J. Am. Chem. Soc.* **1958**, *80*, 3426. (b) Zollinger, H.; Büchler, W.; Wittwer, C. *Helv. Chim. Acta* **1953**, *36*, 1711.

(5) (a) Bunton, C. A.; Ohmenzetter, K.; Sepulveda, L. *J. Phys. Chem.* **1977**, *81*, 2000. (b) Bunton, C. A.; Hong, Y. S.; Romsted, L. S. In *Solution Behavior of Surfactants*; Mittal, K. L.; Fendler, E. J., Eds.; Plenum: New York, 1982; Vol. 2, p 1137.

(6) (a) Crosby, J.; Stirling, C. J. M. *J. Chem. Soc. B* **1970**, 671, 679. (b) Marshall, D. R.; Thomas, P. J.; Stirling, C. J. M. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1914.

(7) Jaeger, D. A.; Robertson, R. E. *J. Org. Chem.* **1977**, *42*, 3298.

(8) Neubert, M. E.; Laskos, S. J., Jr.; Griffith, R. F.; Stahl, M. E.; Maurer, L. J. *Mol. Cryst. Liq. Cryst.* **1979**, *54*, 221.

(9) Johnson, J. R.; Sandborn, L. T. In *Organic Syntheses*; Wiley: New York, 1932; Collect. Vol. I, p 111.

25 °C and filtered. The filtrate was adjusted to pH 4 with concentrated sulfuric acid, and then a solution of 1.7 g (20 mmol) of $NaNO_3$ in 20 mL of H_2O was added. The resultant mixture was extracted with two 20-mL portions of $CHCl_3$, and the combined extracts gave 0.60 g (96%) of the crude product, which on recrystallization at 4 °C from 24 mL of 15:1 (v/v) EtOAc–EtOH yielded **1**: mp 190–191 °C (sealed tube); ^{1}H NMR δ 6.88–7.86 (m, 8 H, Ar H), 4.40 (t, $J = 6$ Hz, 2 H, CH_2O), 3.76 (s, 9 H, $(CH_3)_3N^+$), 3.60 (t, $J = 6$ Hz, CH_2SO_2), 2.71 (t, $J = 8$ Hz, 2 H, CH_2Ar), 1.63 (br m, 2 H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2Ar}$), 1.25 (s, 18 H, $(CH_2)_9$), 0.87 (t, 3 H, CH_3); ^{13}C NMR δ 158.33, 150.04, 140.30, 136.72, 129.33, 127.97, 121.42, 115.76, 61.94, 57.29, 55.44, 35.90, 31.82, 31.06, 29.56, 29.37, 29.27, 29.21, 22.61, 14.07; IR (Nujol) 3040 (m), 1593 (m), 1510 (s), 1335 (vs), 1259 (s), 1193 (m), 1140 (s), 1085 (m), 1013 (m), 955 (m), 832 (s), 787 (w), 714 cm^{-1} (m); cmc = 7.6×10^{-5} M in 0.01 M $MeCO_2H$ at 25 °C; FAB HRMS, calcd for $C_{29}H_{46}NO_3S$ (cation) 488.3200, found 488.3213. Anal. Calcd for $C_{29}H_{46}N_2O_6S\cdot 0.5H_2O$: C, 62.22; H, 8.46. Found: C, 62.09; 62.04; H, 8.39, 8.39.

1-Dodecyl-4-[(2-phenoxyethyl)thio]benzene (6). To 96 mL of 0.25 M NaOEt–EtOH (24 mmol) was added 6.71 g (24.1 mmol) of **3**, followed by 4.84 g (24.1 mmol) of $BrCH_2CH_2OPh$ (Aldrich). The mixture was refluxed for 1 h, added to 200 mL of saturated NaCl–H_2O, and extracted with three 100-mL portions of CH_2Cl_2. The combined extracts yielded 9.1 g of the crude product, which on recrystallization from 100 mL of EtOH and then from 150 mL of hexane gave 6.0 g (62%) of **6**: mp 64–65 °C; ^{1}H NMR δ 6.79–7.39 (m, 9 H, Ar H), 4.12 (t, $J = 7$ Hz, 2 H, CH_2O), 3.24 (t, $J = 7$ Hz, 2 H, CH_2S), 2.57 (t, $J = 7$ Hz, 2 H, CH_2Ar), 1.57 (br m, 2 H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2Ar}$), 1.25 (s, 18 H, $(CH_2)_9$), 0.88 (t, 3 H, CH_3); IR (KBr) 2955 (w), 2915 (s), 2845 (s), 1597 (m), 1492 (m), 1462 (m), 1384 (w), 1287 (w), 1249 (s), 1172 (m), 1079 (m), 1010 (m), 880 (w), 800 (w), 744 (s), 686 cm^{-1} (m). Anal. Calcd for $C_{26}H_{38}OS$: C, 78.34; H, 9.61. Found: C, 78.33; H, 9.61.

1-Dodecyl-4-[(2-phenoxyethyl)sulfonyl]benzene. A mixture of 7.22 g (18.1 mmol) of **6**, 7.1 mL of 31% H_2O_2–H_2O (72 mmol), and 60 mL of glacial $MeCO_2H$ was refluxed for 1 h. Then 75 mL of H_2O was added, and the mixture was extracted with three 100-mL protions of $CHCl_3$. The combined extracts yielded 7.4 g of the crude product, which on recrystallization from hexane yielded 6.9 g (89%) of the title sulfone: mp 87–88 °C; ^{1}H NMR δ 6.60–7.87 (m, 9 H, Ar H), 4.35 (t, $J = 6$ Hz, 2 H, CH_2O), 3.58 (t, $J = 6$ Hz, 2 H, CH_2SO_2), 2.70 (t, $J = 8$ Hz, 2 H, CH_2Ar), 1.64 (br m, 2 H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2Ar}$), 1.26 (s, 18 H, $(CH_2)_9$), 0.88 (t, 3 H, CH_3); IR (KBr) 2955 (w), 2920 (s), 2847 (s), 1598 (m), 1499 (m), 1465 (m), 1390 (w), 1323 (s), 1313 (s), 1293 (s), 1253 (s), 1178 (m), 1136 (s), 1086 (m), 1014 (m), 885 (m), 750 cm^{-1} (m). Anal. Calcd for $C_{26}H_{38}O_3S$: C, 72.51; H, 8.89. Found: C, 72.35; H, 8.79.

Potassium 4-[2-[(4-Dodecylphenyl)sulfonyl]ethoxy]benzenesulfonate (2). A mixture of 0.50 g (1.2 mmol) of the above sulfone and 2.8 g (27 mmol) of concentrated sulfuric acid was stirred vigorously at 25 °C for 1 h and then added to 20 mL of H_2O. The resultant mixture was neutralized to pH 3 at 25 °C with 10% KOH–H_2O and lyophilized. The residue was slurried in 200 mL of 1:1 (v/v) MeOH–CH_2Cl_2 and filtered through 10 g of Celite. Rotary evaporation left the crude product, which was recrystallized from 20 mL of MeOH to give 0.21 g (32%) of **2**: mp 250 °C dec (sealed tube); ^{1}H NMR (D_2O, $Me_3Si(CH_2)_3SO_3Na$) δ 6.41–7.74 (m, 8 H, Ar H), 4.12 (br m, 2 H, CH_2O), 3.49 (br m, 2 H, CH_2SO_2), 2.48 (br m, 2 H, CH_2Ar), 1.45 (br m, 2 H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2Ar}$), 1.22 (s, 18 H, $(CH_2)_9$), 0.84 (br m, 3 H, CH_3) [in this and several other spectra, resolution of the signals at δ 4.12, 3.49, and 0.84 into the anticipated triplets was not achieved]; IR (KBr) 2915 (s), 2855 (m), 1602 (m), 1501 (m), 1464 (m), 1308 (m), 1193 (s), 1145 (s), 1092 (w), 1050 (m), 836 (m), 703 cm^{-1} (m); cmc = 4.0×10^{-5} M in 0.01 M $MeCO_2H$ at 25 °C. Anal. Calcd for $C_{26}H_{37}O_6S_2K$: C, 56.90; H, 6.80. Found: C, 57.09; H, 6.83.

2-[(4-Dodecylphenyl)thio]ethanol. To 30.0 mL of 0.67 M NaOEt–EtOH (20.1 mmol) was added 5.57 g (20.0 mmol) of **3**, followed by 2.50 g (20.0 mmol) of $BrCH_2CH_2OH$ (Aldrich). The mixture was refluxed for 1 h, added to 200 mL of saturated NaCl–H_2O, and extracted with three 75-mL portions of CH_2Cl_2. The combined extracts yielded 8.50 g of the crude product, which on recrystallization from hexane gave 4.28 g (66%) of the title alcohol: mp 56.0–56.5 °C; ^{1}H NMR δ 7.22 (AA′BB′, 4 H, Ar H), 3.71 (q, $J = 6$ Hz, 2 H, CH_2O), 3.07 (t, $J = 6$ Hz, 2 H, CH_2S), 2.57 (t, $J = 8$ Hz, 2 H, CH_2Ar), 2.06 (t, $J = 6$ Hz, 1 H, OH), 1.60 (br m, 2 H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2Ar}$), 1.25 (s, 18 H, $(CH_2)_9$), 0.88 (t, 3 H, CH_3); IR (KBr) 3320 (m), 3210 (m), 2958 (w), 2918 (s), 2848 (s), 1494 (m), 1467 (m), 1404 (w), 1293 (w), 1153 (m), 1066 (s), 1013 (w), 997 (w), 805 (m), 715 cm^{-1} (w); EI HRMS, calcd for $C_{20}H_{34}OS$ 322.2330, found 322.2350.

2-[(4-Dodecylphenyl)sulfonyl]ethanol. Oxidation of the preceding alcohol by a literature procedure[10] gave (81%) of crude material that was recrystallized from hexane to yield the title alcohol: mp 46–47 °C; ^{1}H NMR δ 7.39 and 7.83 (AA′XX′, $J_{AX} + J_{AX'} = 8$ Hz, 4 H, Ar H), 4.00 (q, $J = 6$ Hz, 2 H, CH_2O), 3.34 (t, $J = 6$ Hz, 2 H, CH_2SO_2), 2.79 (t, $J = 6$ Hz, 1 H, OH), 2.70 (t, $J = 8$ Hz, 2 H, CH_2Ar), 1.64 (br m, 2 H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2Ar}$), 1.25 (s, 18 H, $(CH_2)_9$), 0.88 (t, 3 H, CH_3); IR (KBr) 3507 (s), 2920 (s), 2853 (s), 1597 (m), 1470 (m), 1410 (m), 1382 (w), 1293 (s), 1233 (m), 1143 (s), 1092 (m), 1052 (m), 1017 (w), 850 (w), 815 (w), 725 cm^{-1} (m). Anal. Calcd for $C_{20}H_{34}O_3S$: C, 67.75; H, 9.77. Found: C, 67.74; H, 9.76.

4-Dodecyl(vinylsulfonyl)benzene (7). With a literature procedure,[11] 0.396 g (1.12 mmol) of the above alcohol was converted into 0.310 g (64%) of 4-n-$C_{12}H_{25}C_6H_4SO_2CH_2CH_2OSO_2Me$. Without purification, 305 mg of this material was added to 4 mL of CH_2Cl_2 containing 89 mg (0.88 mmol) of Et_3N. The mixture was refluxed for 24 h, washed with 5 mL each of 5% hydrochloric acid and H_2O, dried (Na_2SO_4), and rotary evaporated to give 0.219 g of the crude product. Its recrystallization from 4 mL of hexane at 4 °C gave 0.66 g (22%) of **7**: mp 39.0–39.5 °C; ^{1}H NMR δ 7.34 and 7.79 (AA′XX′, $J_{AX} + J_{AX'} = 8$ Hz, 4 H, Ar H), 5.98–6.71 (m, 3 H, $CH{=}CH_2$), 2.68 (t, $J = 8$ Hz, 2 H, CH_2Ar), 1.62 (br m, 2 H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2Ar}$), 1.25 (s, 18 H, $(CH_2)_9$), 0.88 (t, 3 H, CH_3); IR (KBr) 2925 (s), 2859 (s), 1599 (m), 1465 (m), 1411 (w), 1383 (w), 1323 (s), 1152 (s), 1092 (m), 972 (m), 737 (s), 673 cm^{-1} (m). Anal. Calcd for $C_{20}H_{32}O_2S$: C, 71.38; H, 9.58. Found: C, 71.35; H, 9.64.

(4-Hydroxyphenyl)trimethylammonium Nitrate (8). A mixture of 1.00 g (9.16 mmol) of 4-$NH_2C_6H_4OH$ (Aldrich), 3.11 g (37.0 mmol) of $NaHCO_3$, 4.15 g 32.9 mmol) of $(MeO)_2SO_2$, and 4.6 mL of H_2O was vigorously stirred at 25 °C for 1 h. Solids were removed by filtration, and the filtrate was adjusted to ca. pH 4 with 2 M nitric acid, followed by the addition of 14.3 g (0.168 mol) of $NaNO_3$ in 20 mL of H_2O. By filtration, 0.53 g of crude product was collected, which was recrystallized at 4 °C from EtOH to give 0.25 g (13%) of **8**: mp 185–186 °C; ^{1}H NMR (D_2O, $Me_3Si(CH_2)_3SO_3Na$) δ 7.04 and 7.69 (AA′XX′, $J_{AX} + J_{AX'} = 10$ Hz, 4 H, Ar H), 3.60 (s, 9 H, $(CH_3)_3N^+$); IR (KBr) 3440 (m), 3247 (m), 3110 (s), 3035 (w), 3015 (w), 1618 (m), 1602 (s), 1516 (s), 1460 (w), 1387 (vs), 1297 (s), 1282 (m), 1254 (m), 1228 (s), 1192 (m), 1152 (m), 1127 (m), 1013 (w), 967 (m), 932 (w), 860 (w), 833 (s), 705 cm^{-1} (s). Anal. Calcd for $C_9H_{14}N_2O_4$: C, 50.46; H, 6.59. Found: C, 50.52; H, 6.60.

Sodium 4-[2-[(4-Methylphenyl)sulfonyl]ethoxy]benzenesulfonate (10). 4-$MeC_6H_4SCH_2CH_2OPh$, mp 46–46.5 °C (lit.[12] mp 46 °C), was prepared by a literature procedure[6a] and oxidized with H_2O_2 in $MeCO_2H$ to give 4-$MeC_6H_4SO_2CH_2CH_2OPh$, mp 132–133 °C (lit.[12] mp 135 °C). A mixture of 2.44 g (8.83 mmol) of the sulfone and 4.52 g (44.1 mmol) of concentrated sulfuric acid was stirred for 1 h at 75 °C and then added to 20 mL of H_2O. The resultant solution was adjusted to pH 4 with 15% NaOH–H_2O, extracted with three 30-mL portions of $CHCl_3$, heated to 65 °C (20 mmHg) to remove residual $CHCl_3$, and cooled to 4 °C. The 2.21 g of precipitate was recrystallized from aqueous 0.5% acetic acid to give 1.06 g (32%) of **10**: mp 287–288 °C; ^{1}H NMR (D_2O, $Me_3Si(CH_2)_3SO_3Na$) δ 6.68–7.79 (m, 8 H, Ar H), 4.46 (t, $J = 5$ Hz, 2 H, CH_2O), 3.89 (t, $J = 5$ Hz, 2 H, CH_2SO_2), 2.41 (s, 3 H, CH_3); IR (KBr) 3050 (w), 2920 (m), 1594 (s), 1495 (m), 1460 (w), 1386 (m), 1291 (s), 1182 (vs), 1126 (s), 1085 (w), 1034 (s), 812 (m), 693 cm^{-1} (m); FAB HRMS, calcd for $C_{15}H_{15}O_6S_2$ (anion) 355.0310, found 355.0322. Anal. Calcd for $C_{15}H_{15}O_6S_2Na\cdot 0.25H_2O$: C, 47.05; H, 4.08. Found: C, 46.99, 46.92; H, 4.20, 4.21.

4-Methyl(vinylsulfonyl)benzene (11). With the procedures used for the preparation of **7**, 4-$MeC_6H_4SO_2CH_2CH_2OH$ (Eastman Kodak) was converted (52%) to **11**, mp 65–66 °C (lit.[13] mp 66 °C).

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(10) Schultz, H. S.; Freyermuth, H. B.; Buc, S. R. *J. Org. Chem.* **1963**, *28*, 1140.

(11) Crossland, R. K.; Servis, K. L. *J. Org. Chem.* **1970**, *35*, 3195.

(12) Kader, A. T.; Stirling, C. J. M. *J. Chem. Soc.* **1962**, 3686.

(13) Smith, L. E.; Davis, H. R., Jr. *J. Org. Chem.* **1950**, *15*, 824.

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Stability/Lability Characteristics of 1, 2, and 10 in D_2O. The reaction mixtures contained 0.005 M substrate and, in most cases, an additive, and were monitored by ^1H NMR with $Me_3Si(CH_2)_3SO_3Na$ as internal standard. The results are summarized in Table I. In entries 1 and 5, 1 decomposed to 7 and 8. Due to poor resolution and partial overlap of the SO_2CH_2 with the Me_3N^+ signal, it was indeterminable whether or not partial hydrogen–deuterium exchange within the former group accompanied 1's decomposition. The presence of $ArSO_2CD{=}CH_2$ (**7**-*d*) was likewise uncertain by ^1H NMR. In entries 11 and 12, 2 decomposed to 7 and 9, whose possible deuterium contents were uncertain. The limited solubility of 2 at 25 °C (Kraft temperature >25 °C) precluded the use of more concentrated KOD solutions in cleavage studies. At higher temperatures in such solutions, 2 should undergo rapid cleavage to 7 and 9. In entries 13, 15, and 16, 10 underwent isotopic exchange as it decomposed to 11 and 9 (Na^+). Also, in entries 15 and 16, 7-*d* was detected. In no run was 4-*n*-$C_{12}H_{25}C_6H_4SO_2CDH(D)CH_2OD$ or 4-$MeC_6H_4SO_2CDH(D)CH_2OD$ detected, which would have resulted from Michael-like addition of D_2O to 7 and 11, respectively.

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Registry No. **1**, 103752-44-9; **2**, 103752-45-0; **3**, 20025-90-5; **4**, 57011-90-2; **5**, 103752-35-8; **5** (sulfonyl), 103752-36-9; **5** (sulfonyl amine), 103752-37-0; **6**, 103752-38-1; **6** (sulfonyl), 103752-39-2; **6** (alcohol), 103752-40-5; **6** (sulfonyl alcohol), 103752-41-6; **7**, 60523-06-0; **8**, 92939-04-3; **10**, 103752-46-1; 4-$HOC_6H_4NHCOMe$, 103-90-2; $Br(CH_2)_2Br$, 106-93-4; $Br(CH_2)_2OPh$, 589-10-6; $Br(CH_2)_2OH$, 540-51-2; 4-$C_{12}H_{25}C_6H_4SO_2(CH_2)_2OSO_2Me$, 103752-42-7; 4-$NH_2C_6H_4OH$, 123-30-8; 4-$MeC_6H_4S(CH_2)_2OPh$, 94001-61-3; 4-$MeC_6H_4SO_2(CH_2)_2OPh$, 28611-88-3.

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[14] **Note Added in Proof:** At 50 °C in 0.1 M KOD–D_2O, 0.005 M 2 decomposed completely to 7 and 9 within 10 min.

Reactions of Carbenes and Photoexcited Ketones with Phosphorus Compounds

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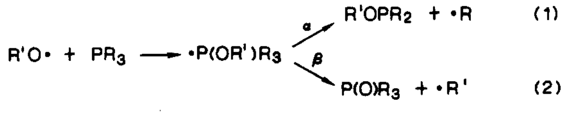
The photoinduced reactions of aromatic carbonyl compounds and diaryldiazomethanes with phosphorus derivatives were investigated by EPR and laser flash photolysis techniques. Triplet ketones reacted with tetraethyl pyrophosphite via a mechanism akin to a homolytic displacement (S_H2) process at an almost diffusion controlled rate ($k_{300} = (7.96 \pm 0.04) \times 10^8\ M^{-1}\ s^{-1}$ for benzophenone). Triplet benzophenone reacted very rapidly with tetraphenyldiphosphine ($k_{300} = 2 \times 10^8\ M^{-1}\ s^{-1}$). Tetraethyl pyrophosphite also underwent homolytic attack by triplet diphenylcarbene ($k_{300} = (7.4 \pm 0.7) \times 10^6\ M^{-1}\ s^{-1}$) to give a diradical intermediate (or transition state) which, by β-fragmentation, gave $Ph_2\dot{C}OP(O)(OEt)_2$. Product studies supported the proposed mechanism. In contrast with diphenylcarbene, fluorenylidene appeared to react via a nonradical mechanism.

Tervalent phosphorus compounds, PR_3, undergo attack by oxygen-centered radicals, $^\bullet OR'$, to give phosphoranyl intermediates, which have been often detected by EPR.[1] The phosphoranyl radicals decompose by cleavage either of one of the P–R bonds (α-scission) or of the O–R′ bond (β-scission).[2,3] For the α-scission the overall reaction amounts to a homolytic substitution S_H2 of R by OR′ (eq 1), while in the latter case oxidation of the tervalent to a pentavalent phosphorus occurs (eq 2). The relative importance with which one of the two routes is chosen depends essentially on the relative strength of the P–R and O–R′ bonds; thus, for R = Ph and R′ = *t*-Bu, triphenylphosphine oxide is obtained in high yield (reaction 2), while if R′ is a primary or secondary alkyl group variable amounts of substitution and oxidation products are recovered depending on the nature of the alkyl.[2,3]



Tervalent phosphorus compounds are also attacked by carbon centered radicals to give phosphoranyls, which may subsequently undergo α- or β-scission. The latter route is generally observed when reacting phenyl or vinyl radicals with phosphites.[3] Reaction 3 also occurs slowly with R′ = methyl or isopropyl. However, *tert*-butyl radicals do not react readily with phosphites.[2]

$$^\bullet R' + P(OR)_3 \rightarrow {}^\bullet P(OR)_3R' \rightarrow (O)P(OR)_2R' + {}^\bullet R \qquad (3)$$

In principle, homolytic displacement or oxidation could be brought about by other species containing unpaired electrons, such as triplet state molecules. We are not aware of any reports of homolytic reactions of the kind described in eq 1–3 which are carried out by triplet analogues of alkoxyl radicals, e.g., excited ketones, or triplet analogues

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[1] Roberts, B. P. In *Advances in Free Radical Chemistry*; Williams, G. H., Ed.; Heyden: London, 1980; Vol. 6, p 225.

[2] Ingold, K. U.; Roberts, B. P. In *Free Radical Substitution Reactions*; Wiley-Interscience: New York, 1971; pp 116–133.

[3] Bentrude, W. G. In *Free Radicals*; Kochi, J. K., Ed.; Wiley-Interscience: New York, 1973; Vol. II, pp 595–663.

0022-3263/86/1951-3959$01.50/0