2.85–3.10 (m, 2 H, CH_2S), 4.10–4.30 (m, 2 H, CH_2O). Anal. Calcd for $C_8H_{12}OS$ (156.3): C, 61.49; H, 7.74. Found: C, 61.10; H, 7.88.

2,3-Diphenyl-5,6-dihydro-1,4-oxathiin (7b). **7b** was isolated by liquid chromatography (silica gel 32-100, toluene): yield, 85% (from the **6b**/**7b** mixture, see above); mp 59–60 °C; IR (KBr) 3020, 3060, 3080 (=CH), 1595 and 1570 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.04 (td, $\sum J$ = 9 Hz, 2 H, CH_2S), 7.08 (m, 10 H, Ph); ^{13}C NMR ($CDCl_3$) δ 27.76 (CH_2S), 65.50 (CH_2O), 107.54 (=CRS), 127.03 and 127.30 (para C of Ph), 127.44 and 128.07 (meta C of Ph), 129.05 and 130.21 (ortho C of Ph), 136.31 and 138.68 (C_1 of Ph), 145.83 (=CRO); MS (70 eV), *m/e* (relative intensity) 254 (61.9, M^+), 226 (4.5, $M^+ - C_2H_4$), 121 (100, $PhCS^+$), 105 (70.0, $PhCO^+$), 77 (28.3, $C_6H_5^+$), 51 (7.0, $C_4H_3^+$). Anal. Calcd for $C_{16}H_{14}OS$ (254.4): C, 75.55; H, 5.55. Found: C, 75.36; H, 5.42.

Acknowledgment. Support of this work by the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

Registry No. 1, 6478-04-2; **2a** (X = Cl), 4091-39-8; **2b** (X = Cl), 694-28-0; **2c** (X = Cl), 822-87-7; **2c** (X = Br), 822-85-5; **2c** (X = CF_3CO_2), 66197-69-1; **2d** (X = Br), 1484-50-0; **3a** (X = Cl), 101249-19-8; **3b** (X = Cl), 101249-20-1; **3c** (X = Cl), 101249-21-2; **3c** (X = Br), 101249-22-3; **3c** (X = CF_3CO_2), 101249-23-4; **3d** (X = Br), 101249-24-5; **4a**, 101249-27-8; **4b**, 101315-92-8; **4c**, 101249-28-9; **4d**, 101249-29-0; **5**, 60-24-2; **6a**, 101249-25-6; **6b**, 101249-26-7; **7a**, 35755-85-2; **7b**, 58041-19-3; **9**, 26226-64-2; 1-mercapto-3-chloro-2-propanol, 6478-05-3.

Syntheses of New Substituted Pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecanes: A Novel Synthesis of Hexacyclo[6.2.1.1^{3,6}.0^{2,7}.0^{4,10}.0^{5,9}]dodecane (1,3-Bishomopentaprismane)

Alan P. Marchand* and An-hsiang Wu

Department of Chemistry, North Texas State University, Denton, Texas 76203-5068

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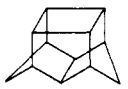
Recently, substituted 1,3-bishomopentaprismanes have attracted attention as intermediates in the synthesis of [4]peristylane and related compounds.[1-3] As part of a program that is involved with the synthesis and chemistry of new, substituted pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecanes,[4-10] we now report several new derivatives of this system that lead to a novel synthesis of the parent 1,3-bishomopentaprismane (**1**).



1

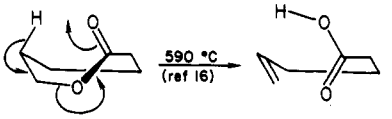
Compound **1** has been synthesized previously: (i) via [2 + 2] photocylization of isodrin followed by dechlorination of the resulting photoadduct,[11] and (ii) as a by-product that accompanies the solvolysis of any of several octahydrodimethanonaphthyl brosylates.[12] In all such cases, Diels–Alder cycloadditions of substituted cyclopentadienes with appropriately substituted norbornenes and/or norbornadienes furnish the required dimethanonaphthalene skeleton. The present synthesis of **1** is novel in that the hexacyclic ring system is formed from an appropriately substituted pentacyclic precursor (i.e., **6**).

Our approach to the synthesis of **1** is shown in Scheme I. The readily available[4] pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]-undecane-8,11-dione (**2**) was chosen as starting material for this study. Symmetrical diketone **2** could be converted into unsymmetrical enone **3** in two ways. First, **3** could be synthesized directly via Wadsworth–Emmons reaction of **2** with the ylide derived from ethyl (diethoxyphosphinyl)acetate.[13,14] Alternatively, Reformatsky reaction[15] of **2** with $BrZnCH_2CO_2Et$ afforded **4**, which was then converted to the corresponding mesylate; subsequent DBU-promoted elimination of methanesulfonic acid from this intermediate afforded **3**.

Interestingly, reduction of **3** with sodium borohydride in methanol at 0 °C resulted in regiospecific reduction via exclusive attack at the exo face of the ketone carbonyl group. Subsequent transannular Michael addition of the resulting endo alcohol to the proximate α,β-unsaturated ester moiety then afforded the observed product, **5**. Alternatively, catalytic hydrogenation of **3** simply resulted in reduction of its carbon–carbon double bond, thereby affording **6**.

Reaction of **6** with sodium borohydride in methanol at 0 °C resulted again in regiospecific reduction via exclusive exo attack at the ketone carbonyl group. Subsequent transannular transesterification between the resulting endo alcohol and the proximate ester moiety afforded one of the observed reaction products, lactone **7**. Lactol **8** was also produced in this reaction, presumably via further reaction of **7** with excess sodium borohydride. The structure of **8** was established via dehydration to the corresponding vinyl ether **9**.

Flash vacuum pyrolysis of **7** at 700 °C resulted in elimination of carbon dioxide with concomitant formation of 1,3-bishomopentaprismane (**1**). It should be noted that **7** contains a substituted ϵ-caprolactone moiety. Flash vacuum pyrolysis of the parent, unsubstituted ϵ-caprolactone has been studied by Bailey and Bird;[16] pyrolysis of this compound at 590 °C was observed to afford 5-hexenoic acid in 53% yield. Presumably, ϵ-caprolactone is sufficiently flexible that normal ester pyrolysis occurs, resulting in β-elimination via a quasi-six-membered ring transition state[16] (eq 1). Such flexibility is not present



(1)

in **7**, nor is alkene formation (via β-elemination) likely to occur in this strained cage system (Scheme II). To our knowledge, the formation of **1** from **7** represents the first example wherein pyrolysis of a substituted ϵ-caprolactone results in fragmentation with elimination of carbon dioxide

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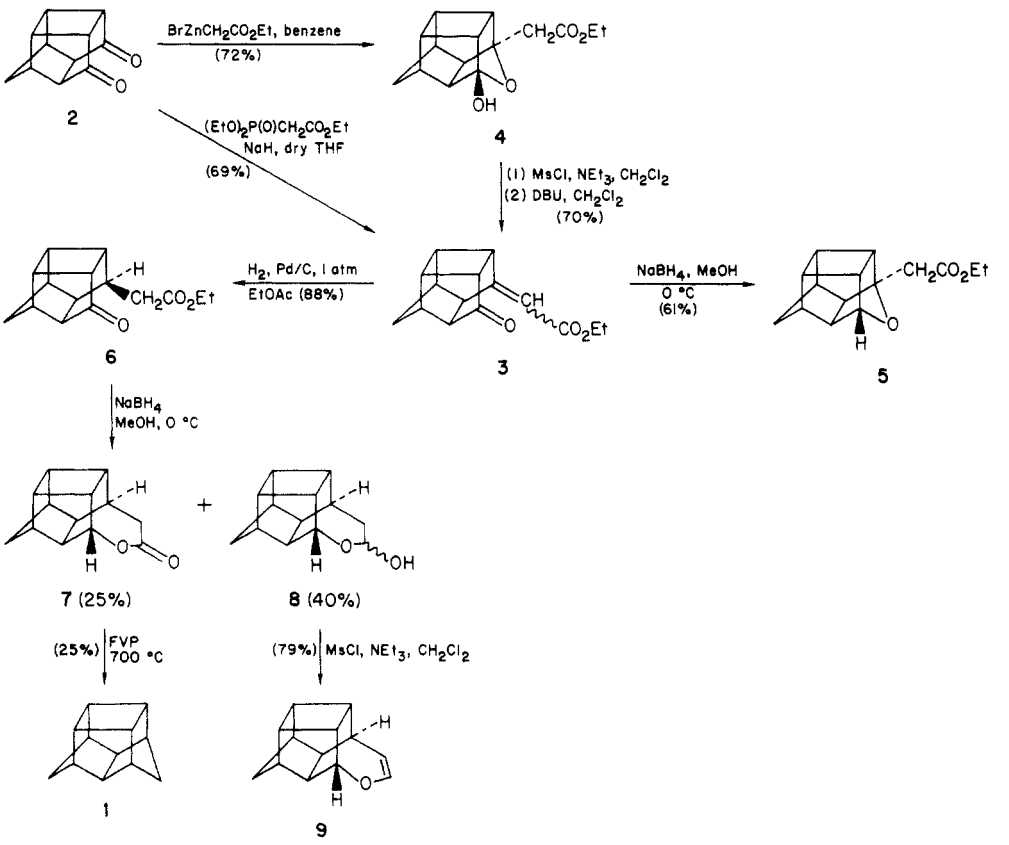
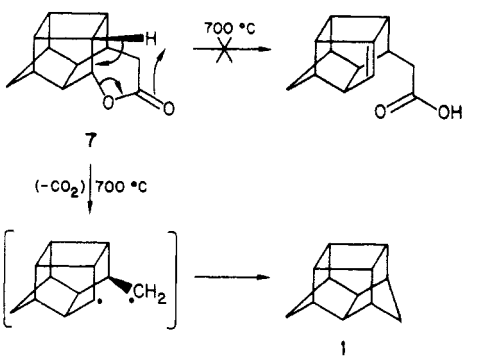
Scheme I



Scheme II



and concomitant formation of a substituted cyclopentane.

Experimental Section

Melting points and boiling points are uncorrected. Proton NMR spectra (60 MHz) and ^{13}C NMR spectra were obtained on $CDCl_3$ solutions that contained 1% (v/v) tetramethylsilane as internal standard; signals are reported in parts per million (δ) downfield from internal tetramethylsilane. High-resolution mass spectra were obtained at the Midwest Center for Mass Spectrometry, Department of Chemistry, University of Nebraska, Lincoln, NE.

Synthesis of 3. Method A. To a mixture of activated zinc,[17] (30.0 g, 0.459 mol, excess), dry benzene (100 mL), and a catalytic amount of iodine was added ethyl bromoacetate (30.6 g, 0.183 mol) dropwise with stirring under nitrogen during 30 min. The reaction mixture was allowed to stir for an additional 30 min after the addition of ethyl bromoacetate had been completed. To this mixture was then added a solution of diketone **2** (32.0 g, 0.183 mol) in dry benzene (200 mL) dropwise with stirring under nitrogen during 1.5 h. After the addition had been completed, the reaction mixture was heated to reflux, and stirring was continued for 6 h. The reaction mixture was then concentrated in vacuo, and to the residue was added a mixture of methanol (50 mL), acetic acid (50 mL), water (50 mL), and ether (200 mL). The resulting mixture was stirred for 30 min and then transferred into a separatory funnel. The layers were separated, and the organic layer was washed with saturated aqueous sodium carbonate solution until the water layer became neutral. The organic layer was dried (anhydrous magnesium sulfate) and filtered, and the filtrate was then concentrated in vacuo. The residue was distilled in vacuo, thereby affording a colorless oil (**4**, 34.5 g, 72%): bp 165–167 °C (0.05 mm); IR (neat) 3375 (s), 2935 (s), 2875 (m), 1720 cm^{-1} (s); ^1H NMR δ 1.12 (t, J = 7.2 Hz, 3 H), 1.38 (*AB*, J_{AB} = 10.5 Hz, 1 H), 1.74 (*AB*, J_{AB} = 10.5 Hz, 1 H), 2.35–2.53 (m, 8 H), 2.65 (s, 2 H), 4.00 (q, J = 7.2 Hz, 2 H), 5.28 (s, 1 H); ^{13}C NMR δ 13.9 (q), 38.4 (t), 41.7 (d), 43.1 (d), 43.6 (d), 44.9 (d), 45.7 (d), 47.2 (d), 47.9 (d), 57.4 (d), 58.2 (t), 60.4 (t), 88.6 (s), 118.2 (s), 170.1 (s); mass spectrum (70 eV), m/e (relative intensity) 262.1 (molecular ion, 14.5), 244.1 (26.6), 198.1 (39.4), 188.1 (97.8), 143.1 (80.3), 129.1 (79.8), 91.0 (100).

Anal. Calcd for $C_{15}H_{18}O_4$: C, 68.69; H, 6.92. Found: C, 68.69; H, 7.20.

A mixture of **4** (36.0 g, 0.137 mol), triethylamine (16.7 g, 0.165 mol), and methylene chloride (100 mL) was cooled to 0 °C via application of an external ice bath. To this cooled mixture was added a solution of methanesulfonyl chloride (16.0 g, 0.139 mol) in methylene chloride (100 mL) dropwise with stirring under nitrogen during 30 min. After the addition had been completed, the ice bath was removed, and the reaction was stirred at ambient temperature under nitrogen for 3.5 h. Saturated aqueous ammonium chloride solution (200 mL) was then added, and the resulting mixture was extracted with methylene chloride (3 × 100 mL). The combined extracts were dried (anhydrous magnesium sulfate) and filtered, and the filtrate was concentrated in vacuo to a volume of 100 mL. To this solution (which contained the crude *O*-mesyl derivative of **4**) was added a solution of diazabicyclo[5.4.0]undec-7-ene (DBU, 25.0 g, 0.16 mol) in dry methylene chloride (50 mL) dropwise with stirring under nitrogen during 30 min. After the addition had been completed, the resulting mixture was stirred under nitrogen for 8 h. The reaction mixture was then extracted with saturated aqueous ammonium chloride solution (3 × 100 mL). The combined extracts were dried (an-

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hydrous magnesium sulfate) and filtered, and the filtrate was concentrated in vacuo. The residual oil was distilled in vacuo, thereby affording **3** (mixture of *Z* and *E* isomers) as a colorless oil (23.3 g, 70%): bp 106–107 °C (0.05 mm); IR (neat) 3050 (m), 2950 (s), 2880 (m), 1720 (s), 1650 cm^{-1} (m); ^1H NMR δ 1.08 (t, J = 7.2 Hz, 3 H, 1.59 (*AB*, J_{AB} = 10.5 Hz, 1 H), 1.86 (*AB*, J_{AB} = 10.5 Hz, 1 H), 2.53–2.67 (m, 6 H), 2.98 (s, 1 H), 3.93 (q, J = 7.2 Hz, 2 H), 3.97–4.00 (m, 1 H), 5.47 (s, 1 H); ^{13}C NMR δ 14.0 (q), 36.8 (t), 38.9 (d), 41.7 (d), 43.3 (d), 44.7 (d), 45.2 (d), 47.3 (d), 48.5 (d), 54.5 (d), 59.5 (t), 111.4 (d), 161.4 (s), 165.5 (s), 215.0 (s); mass spectrum (70 eV), m/e (relative intensity) 244.1 (molecular ion, 4.1), 198.1 (100), 170.1 (44.8), 141.1 (27.9), 128.0 (33.2), 118.0 (43.3), 115.0 (31.3), 91.0 (18.3).

Anal. Calcd for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60. Found: C, 73.51; H, 6.92.

Method B. To a suspension of sodium hydride (2.4 g, 100 mmol) in dry tetrahydrofuran (THF, 20 mL) was added ethyl (diethoxyphosphinyl)acetate (11.21 g, 50.0 mmol) dropwise with stirring under nitrogen during 30 min. After the addition had been completed, the reaction mixture was stirred at ambient temperature for 30 min. A solution of **2** (8.71 g, 50.0 mmol) in dry THF (80 mL) was added dropwise with stirring under nitrogen during 2 h. After the addition of **2** had been completed, the resulting mixture was refluxed with stirring for 4 h. The reaction mixture was then cooled, and saturated ammonium chloride solution (200 mL) was then added. The resulting mixture was transferred into a separatory funnel and extracted with ether (3 × 50 mL). The combined ethereal layers were dried (anhydrous magnesium sulfate) and filtered, and the filtrate was concentrated in vacuo. The oily residue was distilled in vacuo, thereby affording **3** (mixture of *Z* and *E* isomers) as a colorless oil (8.4 g, 69%), bp 106–107 °C (0.05 mm).

Reduction of 3 with Sodium Borohydride in Methanol. A stirred solution of **3** (1.22 g, 5.0 mmol) in methanol (20 mL) under nitrogen was cooled to 0 °C via application of an external ice bath. To this cooled, stirred solution was added sodium borohydride (0.76 g, 20 mmol) slowly and in sufficiently small portions to permit the reaction temperature to be maintained near 0 °C throughout the time of addition. After the addition of sodium borohydride had been completed, the cold bath was removed, and the reaction was stirred under nitrogen at ambient temperature for 6 h. Saturated aqueous ammonium chloride solution (50 mL) was then added, and the resulting mixture was transferred into a separatory funnel and extracted with ether (3 × 20 mL). The combined ethereal extracts were dried (anhydrous magnesium sulfate) and filtered, and the filtrate was concentrated in vacuo. The oily residue was then distilled in vacuo, thereby affording **5** as a colorless oil (0.75 g, 61%), bp 126–126 °C (0.04 mm): IR (neat) 2970 (s), 2860 (m), 1725 cm^{-1} (s); ^1H NMR δ 1.03 (t, J = 7.2 Hz, 3 H), 1.12 (*AB*, J_{AB} = 13 Hz, 1 H), 1.65 (*AB*, J_{AB} = 13 Hz, 1 H), 2.19–2.62 (m, 10 H), 3.93 (q, J = 7.2 Hz, 2 H), 4.52 (t, J = 9.0 Hz, 1 H); ^{13}C NMR δ 13.8 (q), 37.8 (t), 40.9 (d), 41.5 (d), 43.2 (d), 43.3 (d), 44.2 (d), 44.6 (d), 46.7 (d), 55.3 (d), 57.4 (d), 59.8 (t), 85.1 (d), 92.8 (s), 170.1 (s); mass spectrum (70 eV), m/e (relative intensity) 246.1 (molecular ion, 6.2), 172.0 (100), 159.0 (85.7), 131.0 (25.9), 129.0 (20.8).

Anal. Calcd for $C_{15}H_{18}O_3$: C, 73.15; H, 7.37. Found: C, 72.83; H, 7.22.

Catalytic Hydrogenation of 3. A mixture of **3** (5.6 g, 23 mmol) and 5% palladium on charcoal (1.5 g) in ethyl acetate (150 mL) was purged with a stream of nitrogen for 30 min. The resulting mixture was stirred, and hydrogen gas was passed through the reaction mixture for 24 h. The reaction mixture was then filtered, and the filtrate was concentrated in vacuo. The oily residue was distilled in vacuo, thereby affording **6** (5.0 g, 88%) as a colorless oil, bp 124–125 °C (0.05 mm): IR (neat) 2980 (s), 2860 (m), 1720 cm^{-1} (s); ^1H NMR δ 1.02 (t, J = 7.2 Hz, 3 H), 1.34 (*AB*, J_{AB} = 11 Hz, 1 H), 1.61 (*AB*, J_{AB} = 11 Hz, 1 H), 2.16–2.52 (m, 11 H), 3.88 (q, J = 7.2 Hz, 2 H); ^{13}C NMR δ 13.7 (q), 31.5 (t), 35.4 (d), 36.8 (d), 39.0 (d), 41.6 (d), 41.8 (d), 42.3 (d), 43.1 (d), 47.8 (d), 50.0 (d), 51.6 (t), 59.6 (t), 171.9 (s), 219.1 (s); mass spectrum (70 eV), m/e (relative intensity) 247.1 (3.1), 246.1 (molecular ion, 19.6), 201.1 (20.6), 172.1 (100), 152.1 (32.2), 129.1 (33.9), 107.1 (26.8), 91.1 (54.1).

Anal. Calcd for $C_{15}H_{18}O_3$: C, 73.15; H, 7.37. Found: C, 73.26; H, 7.23.

Reduction of 6 with Sodium Borohydride in Methanol. A stirred solution of **6** (4.8 g, 19.5 mmol) in methanol (60 mL) was cooled to 0 °C via application of an external ice bath. To this stirred, cooled solution was added sodium borohydride (3.0 g, 79 mmol) slowly and in sufficiently small portions to permit the reaction temperature to be maintained near 0 °C throughout the time of addition. After the addition of sodium borohydride had been completed, the cold bath was removed, and the reaction mixture was stirred under nitrogen at ambient temperature for 2 h. Workup was continued in the manner described above for the reduction of **3** with sodium borohydride in methanol. The crude oily product was purified via column chromatography on silica gel (10% ethyl acetate–hexane eluent). Two reaction products were thereby obtained:

(i) Compound **7** (1.0 g, 25%) was obtained as a colorless microcrystalline solid, mp 88–89 °C: IR (KBr) 2980 (s), 2880 (m), 1725 cm^{-1} (s); ^1H NMR δ 1.23 (*AB*, J_{AB} = 11 Hz, 1 H), 1.66 (*AB*, J_{AB} = 11 Hz, 1 H), 2.33–2.94 (m, 11 H), 4.11 (t, J = 1.8 Hz, 1 H); ^{13}C NMR δ 34.4 (t), 35.6 (d), 36.2 (d), 37.7 (d), 38.9 (d), 38.9 (d), 42.5 (d), 44.6 (d), 45.6 (d), 46.6 (t), 77.8 (d), 172.8 (s); mass spectrum (70 eV), m/e (relative intensity) 203.1 (2.3), 202.1 (molecular ion, 14.7), 174.1 (43.8), 156.0 (19.3), 128.0 (26.8), 91.0 (100).

Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 76.94; H, 6.92.

(ii) Compound **8** (1.6 g, 40%) was obtained as a colorless microcrystalline solid, mp 106–107 °C: IR (KBr) 3360 (s), 2960 (s), 2875 cm^{-1} (m); ^1H NMR δ 1.35 (*AB* J_{AB} = 13 Hz, 1 H), 1.75 (*AB*, J_{AB} = 13 Hz, 1 H), 2.16–2.59 (m, 11 H), 3.75–3.80 (m, 1 H), 4.90–5.08 (m, 1 H); ^{13}C NMR δ 35.1 (t), 35.9 (t), 37.0 (d), 38.0 (d), 39.1 (d), 39.9 (d), 42.1 (d), 42.9 (d), 43.9 (d), 46.2 (d), 46.6 (d), 75.6 (d), 95.8 (d); mass spectrum (70 eV), m/e (relative intensity) 204.1 (molecular ion, 3.4), 186.1 (26.7), 158.1 (20.5), 129.1 (21.7), 120.0 (34.4), 115.0 (27.6), 91.1 (100).

Anal. Calcd for $C_{13}H_{16}O_2$: M_r 204.1151. Found (high-resolution mass spectrometry): M_r 204.1157.

The structure of lactol **8** was further established via its facile dehydration to vinyl ether **9**. To a stirred solution of **8** (800 mg, 3.92 mmol) and triethylamine (480 mg, 4.75 mmol) in dry methylene chloride (10 mL) under nitrogen was slowly added a solution of methanesulfonyl chloride (470 mg, 4.10 mmol) in dry methylene chloride (5 mL) dropwise during 30 min. After the addition of methanesulfonyl chloride had been completed, the resulting mixture was stirred under nitrogen at ambient temperature for 8 h. Saturated aqueous ammonium chloride solution (50 mL) was then added, and the resulting mixture was transferred to a separatory funnel and extracted with methylene chloride (3 × 30 mL). The combined organic extracts were dried (anhydrous magnesium sulfate) and filtered, and the filtrate was concentrated in vacuo. The resulting oily residue was distilled in vacuo, thereby affording **9** (0.58 g, 79%) as a colorless oil, bp 112–113 °C (0.1 mm): IR (neat) 3050 (m), 2980 (s), 2880 (m), 1650 cm^{-1} (s); ^1H NMR δ 1.10 (*AB*, J_{AB} = 13 Hz, 1 H), 1.85 (*AB*, J_{AB} = 13 Hz, 1 H), 2.14–2.57 (m, 9 H), 3.75 (m, 1 H), 4.80–5.26 (m, 1 H), 7.10 (s, 1 H); ^{13}C NMR δ 34.7 (t), 38.5 (d), 39.4 (d), 40.1 (d), 43.1 (d), 43.3 (d), 45.9 (d), 46.2 (d), 47.7 (d), 51.9 (d), 79.8 (d), 101.2 (d), 144.5 (d); mass spectrum (70 eV), m/e (relative intensity) 187.1 (5.2), 186.1 (molecular ion, 41.7), 142.1 (10.0), 129.1 (21.7), 120.0 (59.2), 90.1 (100).

Anal. Calcd for $C_{13}H_{14}O$: M_r 186.1045. Found (high-resolution mass spectrometry): M_r 186.1050.

Flash Vacuum Pyrolysis of 7. A small flask containing **7** (7.50 g, 37.1 mmol) was connected to one end of a quartz tube; a receiving flask with a vacuum outlet was connected at the other end of this tube. The quartz tube was preheated in a tube furnace at 700 °C for 30 min, at which time the system was evacuated to 0.01 mm and the receiving flask was cooled by external application of a liquid nitrogen bath. The flask containing **7** was then heated at 200 °C (oil bath); heating was continued until all of the starting material had sublimed. The product that had condensed in the receiving flask was purified via column chromatography on silica gel (hexane eluent). Compound **1** (1.47 g, 25%) was thereby obtained as a colorless waxy solid, mp 163–165 °C (sealed tube) (lit.[12] mp 165–167 °C). Compound **1** is highly volatile, and care must be taken to avoid losses via sublimation during isolation and purification: IR (KBr) 2980 (s), 2880 cm^{-1} (m); ^{13}C NMR 41.2 (t), 44.0 (d), 46.2 (d), 53.4 (d); mass spectrum

(70 eV), *m/e* (relative intensity) 159.0 (12.6), 158.0 (molecular ion, 96.4), 129.0 (19.3), 115.0 (23.0), 92.0 (100).

Acknowledgment. Financial support of our study by the Naval Weapons Center (Grant N60530-85-C-0309), the Air Force Office of Scientific Research, Air Force Systems Command (Grant AFOSR-84-0085), the Robert A. Welch Foundation (Grant B-963), and the North Texas State University Faculty Research Committee is gratefully acknowledged.

Registry No. **1**, 704-02-9; **2**, 2958-72-7; (*Z*)-**3**, 101418-76-2; (*E*)-**3**, 101418-83-1; **4**, 101418-77-3; **4** (mesylate), 101418-82-0; **5**, 101470-91-1; **6**, 101418-78-4; **7**, 101418-79-5; **8**, 101418-80-8; **9**, 101418-81-9; ethyl (diethoxyphosphinyl)acetate, 867-13-0.

Selective Functionalization. 9. The Chlorination of Phenol and Some Phenyl Ethers by Functionalized Surfactants

Samuel O. Onyiriuka and Colin J. Suckling*

Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow G1 1XL, Scotland

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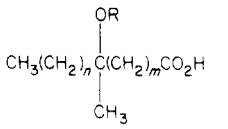
The possiblity that the regioselectivity of organic reactions might be modified advantageously in a micellar environment has been investigated for many systems including aromatic substitution[1-7] and addition to alkenes.[8-10] In our previous studies,[5] we showed that the regioselectivity of the chlorination of phenol was modified in a micellar environment so that ortho chlorination was enhanced. This result was consistent with the time average orientation of phenol in the micellar environment in which the ortho protons occupy the most polar environment as shown by NMR studies.[11] Jaeger and his colleagues showed in a related study that chlorination of pentyl phenyl ether at the para position was promoted in micellar solution,[3] and they have recently extended their study to arylalkyl ethers with longer alkyl chains[6] but without improvement in control of regioselectivity. We also showed that a tertiary alcohol located at C-3 of a stearate molecule (**1a**) in a micellar environment could promote highly regioselective chlorination of phenol in the ortho position.[5] In this paper we report the extension of these experiments to the C-6 functionalized stearate **2a** and to the chlorination of anisole and pentylphenyl ether.

The new C-6 functionalized stearate was prepared by a Grignard reaction on the corresponding ketone which was



	n	*m*		R		R
1	14	1	a	H	b	Me
2	11	4	a	H	b	Me
3	5	10	a	H	b	Me

obtained by the method of Robinson.[12] Phenol was chlorinated in aqueous acetonitrile (9:1 v/v) by using *tert*-butyl hypochlorite as the source of the chlorine. Experiments were carried out in the absence of surfactants and in the presence of sodium dodecylsulfate (SDS) alone and in combination with the stearate derivatives **2a,b**. The total concentration of surfactant was maintained well above the cmc at 300 mM, and the substrate was present in a twofold excess over the chlorinating agent, *tert*-butyl hypochlorite. For those reactions in which a stearate was included, *tert*-butyl hypochlorite was added first followed by the substrate 1 min later. Under these conditions, polychlorination was totally absent, and yields were 40–60% based upon chlorinating agent used, greater than in our previous studies. Products were analyzed by GLC using the excess substrate as an internal standard.

Under the above reaction conditions, the chlorination of phenol alone yielded approximately equal proportions of 2- and 4-chlorophenols (Table I, entry 1). The micellar environment imposed an average orienting effect upon phenol so that the proportion of ortho chlorination was raised (entry 2). A further and substantial enhancement to the selectivity of the reaction was obtained by including the 6-functionalized stearate **2a** in the micellar solution. As the concentration of **2a** was increased, so the selectivity of the reaction rose (entries 3–6) to a maximum of 94% 2-chlorophenol. If the methyl ether of **2a**, **2b**, was used in its place, the chlorination showed the selectivity of an unfunctionalized micelle only. The results follow a similar pattern to those in our previous study using the stearates **1a** and **3a**[5] in which ortho chlorination was promoted by both functionalized surfactants.

The ethers were chlorinated under similar conditions and were introduced into the reaction dissolved in a small volume of acetonitrile to give a homogeneous solution. With anisole as substrate, it was anticipated that the micellar environment would promote ortho chlorination because our NMR studies[11] had shown that the time average orientation of anisole in micellar solution places the ortho protons in the most polar environment as with phenol. The results show a substantial enhancement of ortho chlorination as expected (entries 7 and 8) and parallel those obtained previously for phenol.[5] In contrast, with pentyl phenyl ether as substrate, the opposite time average orientation had been observed,[11] and accordingly, enhanced para chlorination would be expected. Once again, the results confirmed the expectation (entries 12 and 13) and showed a similar pattern of behavior to that described by Jaeger's group.[3] Our intention to investigate the course of chlorination mediated by the functionalized stearic acids **1–3** was that the tertiary hypochlorites produced by exchange with *tert*-butyl hypochlorite would be localized in a specific micellar environment close to the head groups (**1**) or within the hydrophobic region (**3**) or in an intermediate region (**2**). This localization of the reagent might then lead to pronounced changes in regioselectivity of chlorination if the less substrates were solublized in an organized manner by the micelle but

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