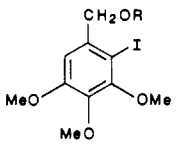
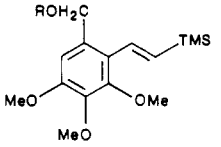
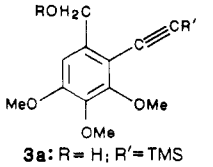
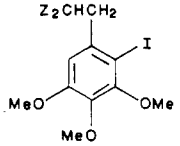
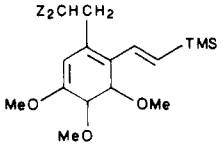
Table I

entry	aryl iodide	product	method	yield, %
1			*a*	93
	1a: R = H	**2a**: R = H		
2	**1b**: R = TMS	**2b**: R = TMS	*a*	93
3	**1a**		*b*	90
		3a: R = H; R′ = TMS		
4	**1b**	**3b**: R = R′ = TMS	*b*	92
5	**1b**	**3c**: R = TMS; R′ = TBDMS	*c*	95
6			*d*	69
	4	**5**		

Z = COOtBu

[a] $Pd(OAc)_2$, Ph_3P, $(CH_3CH_2)_3N$, CH_2CHTMS, Δ, 2 days. [b] $Pd(OAc)_2$, Ph_3P, CHCTMS, $(CH_3CH_2)_3N$, Δ, 2 days. [c] $Pd(OAc)_2$, Ph_3P, CHCTBDMS, $(CH_3CH_2)_3N$, Δ, days. [d] $Pd(OAc)_2$, Ph_3P, CH_2CHTMS, $(CH_3CH_2)_3N$, CuI, Δ, 6 days.

(s, 1 H), and 6.95 (d, $J \sim 20$ Hz, 1 H).

2-[2-(Trimethylsilyl)ethynyl]-3,4,5-trimethoxybenzenemethanol (3a). Palladium(II) acetate, 0.0063 g (2.8×10^{-5} mol, 5.6 M %), was added to a room temperature solution containing 0.0126 g (4.80×10^{-5} mol, 9.5 M %) of triphenylphosphine, 0.07 g (8×10^{-4} mol, 1.5 M %) of (trimethylsilyl)acetylene, and 0.20 g (5.05×10^{-4} mol, 100 M %) of the aryl iodide **1a** in 5.0 mL of dry, degassed triethylamine. The reaction mixture was then heated at reflux for 2 h. Over the course of the reaction, a black precipitate of triethylammonium iodide was formed. The reaction was processed to give the product **3a** cleanly and in high yield, >90%: IR 3750–3300 (broad), 2980, 2140, 1600, 1500, 1470, 1410, 1335, 1250, 1195, and 1130 cm^{-1}; NMR δ 0.27 (s, 9 H), 3.82 (s, 3 H), 3.85 (s, 3 H), 3.94 (s, 3 H), 4.72 (brs, 2 H), and 6.78 (s, 1 H); mass spectrum, *m/z* 294 (M^+).

The silyl ether **3b** was prepared from the ether **1b** as follows: 5.62 g (1.42×10^{-2} mol, 100 M %) of iodide **1b**, 0.0639 g (2.85×10^{-4} mol, 2 M %) of palladium(II) acetate, 0.1270 g (4.84×10^{-4} mol, 3.4 M %) of triphenylphosphine, 2.10 g (2.14×10^{-2} mol, 130 M %) of (trimethylsilyl)acetylene, and 30 mL of triethylamine was refluxed for 4.5 h, cooled to room temperature, poured into 100 mL of anhydrous ether, and filtered through Celite. The crude product was distilled in a Kugelrohr oven 60 °C under high vacuum (~0.05 mmHg) to give 4.78 g (92% yield) of the TMS ether **3b**: IR 2960, 2150, 1595, 1485, 1455, 1405, 1330, 1250, 1195, and 1130 cm^{-1}; NMR δ 0.20 (s, 9 H), 0.28 (s, 9 H), 3.82 (s, 3 H), 3.88 (s, 3 H), 3.96 (s, 3 H), 3.78 (s, 2 H), and 6.87 (s, 1 H); mass spectrum, *m/z* 366 (M^+).

2-[2-[(1,1-Dimethylethyl)dimethylsilyl]ethynyl]-3,4,5-trimethoxybenzenemethanol TMS Ether (3c). Palladium(II) acetate, 0.0160 g (7.12×10^{-5} mol, 2 M %), was added to a room-temperature solution containing 0.0318 g (1.21×10^{-4} mol, 3.4 M %) of triphenylphosphine, ~0.54 g of (*tert*-butyldimethylsilyl)acetylene (3.9×10^{-3} mol, 110 M %), and 1.41 g (3.56×10^{-3} mol, 100 M %) of **1b** in 10 mL of degassed triethylamine. The reaction was then heated at reflux for 4 h. After the standard workup and distillation in a Kugelrohr oven, the reaction gave 1.38 g (95% yield) of the product **3c**: NMR δ 0.20 (s, 9 H), 0.22 (s, 6 H), 1.02 (s, 9 H), 3.85 (s, 3 H), 3.89 (s, 3 H), 3.97 (s, 3 H), 4.80 (s, 2 H), and 6.89 (s, 1 H).

Alcohol **3b** was converted into the silyl ether **3c** by treatment with K_2CO_3 in methanol, which afforded **8**. Compound **8** was reacted with TMSCl–pyridine and then BuLi–TBDMSiCl to yield **3c**.

Bis(1,1-dimethylethyl) (*E*)-[[3,4,5-Trimethoxy-2-[2-(trimethylsilyl)ethenyl]phenyl]methyl]propanedioate (5). A solution containing 1.95 g (3.74×10^{-3} mol, 100 M %) of the iodomalonate **4**,[8] 0.0252 g (1.12×10^{-4} mol, 3 M %) of palladium(II) acetate, 0.0682 g (2.24×10^{-4} mol, 6 M %) of tri-*o*-tolylphosphine, 0.75 g (7.47×10^{-3} mol, 200 M %) of vinyltrimethylsilane, and 0.0249 g (1.31×10^{-4} mol, 3.5 M %) of cuprous iodide in 5.0 mL of triethylamine was heated to reflux under argon for 10 days. The reaction turned dark brown, and a precipitate was formed. After 2 days 5.0 mL of triethylamine was added. The crude reaction was placed in ~100 mL of anhydrous ether and filtered through silica (~10 g). The solvent was removed at reduced pressure to afford 1.27 g (69% yield) of styrene: IR 2970, 2935, 1725, 1595, 1490, 1455, 1370, and 1250 cm^{-1}; NMR δ 0.14 (s, 9 H), 1.41 (s, 18 H), 3.05–3.23 (m, 2 H), 3.28–3.45 (m, 1 H), 3.66–3.87 (m, 9 H), 6.26 (d, $J \sim 2$ Hz, 1 H), 6.52 (s, 1 H), and 6.85 (d, $J \sim 20$ Hz, 1 H); mass spectrum, *m/z* 494 (M^+).

Acknowledgment. The work was supported by Cancer Research Coordinating Committee at UCSD.

Registry No. **1a**, 64490-45-5; **16**, 117370-30-6; **2a**, 117370-31-7; **2b**, 117370-32-8; **3a**, 117370-33-9; **3b**, 117370-34-0; **3c**, 117370-35-1; **4**, 117407-47-3; **5**, 117370-36-2; **8**, 117370-37-3; vinyltrimethylsilane, 754-05-2; bis(β,β,β-trichloroethyl) [(2-ethenyl-3,4,5-trimethoxyphenyl)methyl]propanedioate, 117370-38-4; bis(β,β,β-trichloroethyl)propanedioate, 18833-38-0; (trimethylsilyl)acetylene, 1066-54-2; (*tert*-butyldimethylsilyl)acetylene, 86318-61-8.

Homochiral Ketals in Organic Synthesis. Diastereoselective Cyclopropanation of α,β-Unsaturated Ketals Derived from (*S*,*S*)-(-)-Hydrobenzoin[1]

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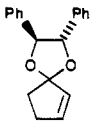
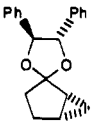
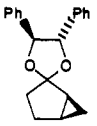
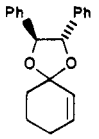
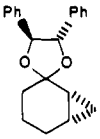
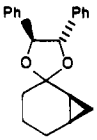
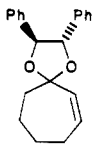
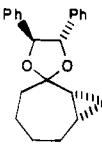
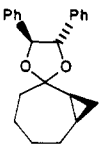
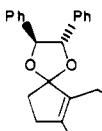
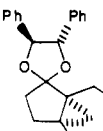
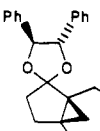
Not long ago we described a general and stereochemically predictable diastereoselective cyclopropanation of

0022-3263/89/1954-0250$01.50/0

Table I

ene ketals	yield,[a] %	mp,[b] °C	cyclopropane ketals	yield,[a] %	diastereomer ratio[c]	mp,[b] °C	$[\alpha]^{25}_D$, deg (c)[b,d]
 1	80	94–97	 2a  2b	66	13:1	106–108	−89.5 (0.42)
 3	87	77–79	 4a  4b	90	19:1	141–142	−74.8 (0.29)
 5	51	oil	 6a  6b	77	15:1	62–65	−104.5 (0.34)
 7	48	46–51	 8a  8b	62	16:1	oil	−46.7 (0.60)

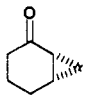
[a] All yields refer to purified compounds. Satisfactory IR and NMR spectra and HRMS or CH analyses were obtained for all compounds. [b] After recrystallization from anhydrous ether. [c] Determined before recrystallization by 62.9-MHz ^{13}C NMR spectroscopy. [d] In $CHCl_3$.

homochiral 2-cycloalken-1-one 1,4-di-*O*-benzyl-L-threitol ketals.[2,3] Diastereoselectivities ranging from 7:1 to 9:1 were commonly observed.[4] The usefulness of this process has been demonstrated in several syntheses.[5] Unfortunately, the diastereoisomers so produced were neither chromatographically separable nor crystalline, and so enantiomerically *pure* cyclopropyl ketones were unavailable by this route. We have examined the suitability of several alternative diols for this process[6,7] and herein report our results for several homochiral 2-cycloalken-1-one (*S,S*)-(−)-hydrobenzoin ketals (Table I).

Ene ketals **1**, **3**, **5**, and **7** were prepared by direct dehydrative ketalization of the corresponding enones[8-10] with (*S,S*)-(−)-hydrobenzoin[11] (PPTS, C_6H_6, heat). Yields and melting points for these ene ketals appear in Table I.

Treatment of ene ketals **1**, **3**, **5**, and **7** with the Simmons–Smith reagent[12] in refluxing diethyl ether provided in good to excellent chemical yields mixtures of cyclopropane ketals **2**, **4**, **6**, and **8**, respectively. In each case diastereoselectivity was greater than 13:1 as determined by 62.9-MHz ^{13}C NMR spectroscopy.[13] Where possible, the mixtures of diastereomeric cyclopropane ketal products were recrystallized from anhydrous ether to give diastereomerically pure compounds. Melting points and rotations for the recrystallized cyclopropane ketal products appear in Table I.

Facial selectivity was determined for the cyclopropanation of 2-cyclohexen-1-one (*S,S*)-(−)-hydrobenzoin ketal (**3**) as follows: hydrolysis of recrystallized **4a** provided (1*R*,6*S*)-bicyclo[4.1.0]heptan-2-one (**9**), $[\alpha]^{25}_D$ +15.6° (*c* 3.7, $CHCl_3$), the rotation of which corresponds to >99% optical purity.[14]



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(1) Portions of this work are taken from the Masters Thesis of Daniel S. Torok, University of Arizona, 1988.

(2) (a) Mash, E. A.; Nelson, K. A. *J. Am. Chem. Soc.* **1985**, *107*, 8256–8258. (b) Mash, E. A.; Nelson, K. A. *Tetrahedron Lett.* **1986**, *27*, 1441–1444.

(3) For a related approach to acyclic cyclopropyl acetals, see: (a) Arai, I.; Mori, A.; Yamamoto, H. *J. Am. Chem. Soc.* **1985**, *107*, 8254–8256. (b) Mori, A.; Arai, I.; Yamamoto, H. *Tetrahedron* **1986**, *42*, 6447–6458.

(4) Mash, E. A.; Nelson, K. A. *Tetrahedron* **1987**, *43*, 679–692.

(5) (a) Nelson, K. A.; Mash, E. A. *J. Org. Chem.* **1986**, *51*, 2721–2724. (b) Mash, E. A.; Fryling, J. A. *J. Org. Chem.* **1987**, *52*, 3000–3003. (c) Mash, E. A. *J. Org. Chem.* **1987**, *52*, 4142–4143. (d) Mash, E. A.; Math, S. K.; Flann, C. J. *Tetrahedron Lett.* **1988**, *29*, 2147–2150.

(6) Mash, E. A.; Nelson, K. A.; Heidt, P. C. *Tetrahedron Lett.* **1987**, *28*, 1865–1868.

(7) Mash, E. A.; Van Deusen, S., unpublished results.

(8) 2-Cyclopenten-1-one and 2-cyclohexen-1-one were purchased from Aldrich Chemical Co. 2-Cyclohepten-1-one was prepared by the method of Garbisch.[9] 2,3,5,6,7,8-Hexahydro-1*H*,4*H*-azulen-1-one was prepared by the method of Magnus.[10]

(9) Garbisch, E. W., Jr. *J. Org. Chem.* **1965**, *30*, 2109–2120.

(10) Cooke, F.; Moerck, R.; Schwindeman, J.; Magnus, P. *J. Org. Chem.* **1980**, *45*, 1046–1053.

(11) (a) Dietl, F.; Haunschild, J.; Merz, A. *Tetrahedron* **1985**, *41*, 1193–1197. (b) Jacobsen, E. N.; Marko, I.; Mungall, W. S.; Schroder, G.; Sharpless, K. B. *J. Am. Chem. Soc.* **1988**, *110*, 1968–1970. Both enantiomers of hydrobenzoin are also available from Aldrich Chemical Co.

(12) Shank, R. S.; Shechter, H. *J. Org. Chem.* **1959**, *24*, 1825–1826.

(13) Authentic diastereomeric mixtures of compounds **2**, **4**, **6**, and **8** were prepared for spectroscopic comparison by direct ketalization of the corresponding cyclopropyl ketones with (*dl*)-hydrobenzoin (PPTS, C_6H_6, heat, $-H_2O$). Resonances employed for determination of diastereomer ratios: compound **2** 23.7 (minor), 23.1 (major); compound **4** 32.7 (major), 33.7 (minor); compound **6** 7.8 (minor), 9.7 (major); compound **8** 85.1 and 85.8 (major), 85.7 and 86.1 (minor). For previous examples of the use of ^{13}C NMR spectroscopy in determining diastereomer ratios, see: Hiemstra, H.; Wynberg, H. *Tetrahedron Lett.* **1977**, 2183–2186.

(14) (a) Johnson, C. R.; Barbachyn, M. R. *J. Am. Chem. Soc.* **1982**, *104*, 4290–4291. (b) Hill, R. K.; Morgan, J. W. *J. Org. Chem.* **1968**, *33*, 927–928.

Enantiomerically pure cyclopropyl ketones are now available via diastereoselective cyclopropanation and recrystallization of 2-cycloalken-1-one hydrobenzoin ketals. Since hydrobenzoin is available in both enantiomeric forms,[11] either enantiomer of a particular cyclopropyl ketone can be prepared via this methodology.[15]

Experimental Section

Benzene and methylene chloride were distilled from calcium hydride, and diethyl ether was distilled from phosphorus pentoxide under an inert atmosphere. Zinc–copper couple was prepared according to the method of Shank and Shechter[12] immediately before use. Melting points were taken on a Thomas Unimelt and are uncorrected. Proton magnetic resonance spectra were recorded at 250 MHz on a Bruker WM-250 NMR spectrometer. Chemical shifts are reported as δ values in parts per million (ppm) from tetramethylsilane. Carbon-13 magnetic resonance spectra were recorded at 62.9 MHz on a Bruker WM-250 spectrometer. Chemical shifts are reported as δ values in parts per million (ppm) from the center line of the chloroform-*d* triplet (77.0 ppm). Mass spectral determinations were performed at The Midwest Center for Mass Spectrometry, an NSF Regional Instrumentation Facility (Grant CHE-0211164). Elemental analyses were performed by Desert Analytics, Tucson, AZ. Infrared spectra were recorded on a Perkin-Elmer Model 983 infrared spectrophotometer. Optical rotations were measured at 589 nm on a Rudolph Research Autopol III polarimeter. Thin-layer chromatographic analyses were performed on Merck silica gel 60 plates (0.25 mm, 70–230 mesh ASTM). Merck silica gel 60 (70–230 mesh ASTM) was used for column chromatography.

General Procedure for Ketalization. To a well-stirred solution of the enone (1.5–4.0 equiv) in dry benzene (4–20 mL/mmol) were added (*S,S*)-hydrobenzoin (1 equiv) and pyridinium *p*-toluenesulfonate (5–10 mol %). The mixture was heated to reflux under argon, and water was removed azeotropically with a Dean–Stark trap. Progress of the reaction was monitored by TLC. Ketalization was terminated by cooling the mixture, which was then diluted with ether, washed with saturated aqueous sodium bicarbonate solution and saturated aqueous sodium chloride solution, dried ($MgSO_4$), and filtered. Volatiles were removed in vacuo, and the residue was chromatographed to provide product.

General Procedure for Simmons–Smith Cyclopropanations. A well-stirred suspension of freshly prepared Zn–Cu couple[12] (600–700 mg/mmol ene ketal) in diethyl ether (1–2 mL/mmol ene ketal) under argon was brought to reflux, and a small crystal of iodine and diiodomethane (5 equiv) were added. After 30 min at reflux the ene ketal was added as a solution in diethyl ether. Progress of the reaction was monitored by TLC and proton NMR spectroscopy. When the reaction was complete, the mixture was cooled to 0 °C and quenched with saturated aqueous sodium carbonate solution (12 equiv). After the mixture was stirred at room temperature for 30 min, the gray-black Zn–Cu couple was removed by filtration and washed well with diethyl ether. The combined organic extracts were washed with saturated aqueous ammonium chloride, saturated aqueous sodium bicarbonate, and saturated aqueous sodium chloride, dried ($MgSO_4$), filtered, and concentrated in vacuo to afford the crude product. Column chromatography on silica gel 60 afforded the pure product as a diastereomeric mixture. Recrystallization from a minimal amount of anhydrous diethyl ether afforded the diastereomerically pure product.

2-Cyclopenten-1-one (*S,S*)-Hydrobenzoin Ketal (1). From 2-cyclopenten-1-one (537 mg, 6.50 mmol), (*S,S*)-hydrobenzoin (500 mg, 2.34 mmol), and pyridinium *p*-toluenesulfonate (25 mg, 0.10 mmol) after 72 h product **1** was obtained as a white solid: mp 91–93 °C; $[\alpha]^{25}_D$ −42.0° (*c* 0.500, $CHCl_3$); yield 519 mg, 1.87 mmol, 80%; IR ($CHCl_3$) 3064, 3030, 3017, 2885, 2351, 2340, 1950, 1880, 1810, 1704, 1615, 1603, 1493, 1453, 1359, 1306, 1236, 1167, 1147, 1077, 1058, 1023, 980, 948, 914, 867, 833, 699, 650 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.3–2.45 (2, m), 2.45–2.58 (2, m), 4.75 (2, s), 5.98–6.02 (1, m), 6.20–6.23 (1, m), and 7.20–7.33 (10, m); ^{13}C NMR ($CDCl_3$) δ 29.7 (CH_2), 35.6 (CH_2), 85.3 (CH), 85.7 (CH), 120.6 (C), 126.7 (CH), 128.2 (CH), 128.4 (CH), 131.1 (CH), 136.1 (C), 136.5 (C), and 137.7 (CH). Anal. Calcd for $C_{19}H_{18}O_2$: C, 81.99; H, 6.52. Found: C, 81.70; H, 6.51.

Bicyclo[3.1.0]hexan-2-one (*S,S*)-Hydrobenzoin Ketal (2). Cyclopropanation of ene ketal **1** (1.00 g, 3.60 mmol) gave **2** as a white solid after chromatography. Yield: 690 mg, 2.36 mmol, 66%. The product was recrystallized from anhydrous ether, giving colorless cubic crystals: mp 106–108 °C; $[\alpha]^{25}_D$ −89.5° (*c* 0.42, $CHCl_3$); IR ($CHCl_3$) 3045, 3034, 3011, 2940, 2871, 1960, 1880, 1810, 1603, 1495, 1453, 1358, 1341, 1305, 1285, 1228, 1222, 1198, 1185, 1123, 1049, 1021, 973, 954, 915, 867, 832, 699, 650 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.50–0.65 (2, m), 1.40–2.04 (6, m), 4.6 (2, dd), and 7.1–7.3 (10, m); ^{13}C NMR ($CDCl_3$) δ 6.9 (CH_2), 16.4 (CH), 23.1 (CH), 24.4 (CH_2), 31.7 (CH_2), 84.9 (CH), 85.3 (CH), 119.6 (C), 126.6 (CH), 126.8 (CH), 128.1 (CH), 128.2 (CH), 128.3 (CH), 136.3 (C), and 136.9 (C); mass spectrum (70 eV), *m/z* (relative intensity) 187 (13), 186 (100), 179 (12), 175 (14), 167 (52), 157 (23), 111 (11), 107 (17), 105 (20), 97 (27), 91 (43); exact mass calcd for $C_{13}H_{14}O$ (M^+ − C_6H_5CHO) 186.1045, obsd 186.1044.

2-Cyclohexen-1-one (*S,S*)-Hydrobenzoin Ketal (3). From 2-cyclohexen-1-one (1.35 g, 14.1 mmol), (*S,S*)-hydrobenzoin (1.5 g, 7.0 mmol), and pyridinium *p*-toluenesulfonate (100 mg, 0.40 mmol) after 48 h product **3** was obtained as a white solid: mp 77–79 °C; $[\alpha]^{25}_D$ −14.8° (*c* 0.655, $CHCl_3$); yield 1.77 g, 6.06 mmol, 87%; IR ($CHCl_3$) 3075, 3064, 3032, 3013, 1950, 1880, 1810, 1649, 1603, 1590, 1495, 1453, 1438, 1395, 1346, 1306, 1232, 1208, 1174, 1115, 1087, 1072, 1058, 1024, 973, 948, 916, 867, 844, 699, 650 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.90–2.20 (2, m), 2.10–2.26 (4, m), 4.82 (2, dd), 5.98 (1, d), 6.14 (1, dt), and 7.22–7.42 (10, m); ^{13}C NMR ($CDCl_3$) δ 20.7 (CH_2), 24.9 (CH_2), 34.9 (CH_2), 84.9 (CH_2), 85.3 (CH_2), 106.5 (C), 126.6 (CH), 126.8 (CH), 128.1 (CH), 128.2 (CH), 128.3 (CH), 128.4 (CH), 133.0 (CH), 136.5 (CH), and 136.8 (C). Anal. Calcd for $C_{20}H_{20}O_2$: C, 82.16; H, 6.90. Found: C, 82.23; H, 6.80.

Bicyclo[4.1.0]heptan-2-one (*S,S*)-Hydrobenzoin Ketal (4). Cyclopropanation of ene ketal **3** (1.10 g, 3.77 mmol) gave **4** as a white solid after chromatography. Yield: 936 mg, 3.05 mmol, 90%. The product was recrystallized from anhydrous ether, giving colorless crystals: mp 141–142 °C; $[\alpha]^{25}_D$ −75.0° (*c* 0.42, $CHCl_3$); IR ($CHCl_3$) 3663, 3066, 3032, 3011, 3009, 2942, 2863, 2355, 1948, 1877, 1807, 1602, 1495, 1454, 1389, 1363, 1186, 1137, 1109, 1095, 1077, 1055, 1041, 1026, 1002, 978, 959, 922, 896, 869, 827, 700, 666, 649, 622 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.35 (1, q), 0.72–0.87 (1, m), 1.18–1.34 (1, m), 1.34–1.55 (3, m), 1.55–1.71 (2, m), 1.71–1.98 (2, m), 4.86 (2, dd), and 7.14–7.35 (10, m); ^{13}C NMR ($CDCl_3$) δ 9.8 (CH_2), 12.5 (C), 20.0 (CH), 20.1 (CH_2), 22.3 (CH_2), 32.7 (CH_2), 85.2 (CH), 85.3 (CH), 110.3 (C), 126.7 (CH), 126.8 (CH), 128.0 (CH), 128.1 (CH), 128.2 (CH), 128.3 (CH), 136.8 (C), and 137.0 (C). Anal. Calcd for $C_{21}H_{22}O_2$: C, 82.33; H, 7.23. Found: C, 82.17; H, 7.35.

2-Cyclohepten-1-one (*S,S*)-Hydrobenzoin Ketal (5). From 2-cyclohepten-1-one (540 mg, 4.91 mmol), (*S,S*)-hydrobenzoin (700 mg, 3.27 mmol), and pyridinium *p*-toluenesulfonate (100 mg, 0.40 mmol) after 48 h product **5** was obtained as viscous clear oil: $[\alpha]^{25}_D$ −27.8° (*c* 0.565, $CHCl_3$); yield 505 mg, 1.65 mmol, 51%; IR ($CHCl_3$) 3065, 3030, 3009, 2932, 1949, 1890, 1800, 1730, 1661, 1603, 1495, 1453, 1400, 1360, 1306, 1281, 1223, 1171, 1111, 1086, 1067, 1025, 977, 916, 876, 807, 791, 699, 668, 666, 650 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.70–1.83 (2, m), 1.94–2.08 (2, m), 2.20–2.29 (2, t), 2.29–2.38 (2, m), 4.80 (2, dd), 6.03–6.10 (2, m), and 7.24–7.40 (10, m); ^{13}C NMR ($CDCl_3$) δ 23.4 (CH_2), 26.7 (CH_2), 27.6 (CH_2), 37.6 (CH_2), 85.0 (CH), 85.5 (CH), 110.0 (C), 126.7 (CH), 126.8 (CH), 128.1 (CH), 128.3 (CH), 133.7 (CH), 134.7 (CH), 136.7 (C), and 136.8 (C); mass spectrum (70 eV), *m/z* (relative intensity) 306 (0.5), 201 (14), 200 (100), 180 (25), 179 (25), 178 (15), 167 (47), 165 (19), 110 (16), 105 (34), 91 (58); exact mass calcd for $C_{21}H_{22}O_2$ 306.1620, obsd 306.1622; calcd for $C_{14}H_{16}O$ (M^+ − C_6H_5CHO) 200.1202, obsd 200.1206.

Bicyclo[5.1.0]octan-2-one (*S,S*)-Hydrobenzoin Ketal (6). Cyclopropanation of ene ketal **5** (373 mg, 1.22 mmol) gave product **6** as a white solid after chromatography. Yield: 265 mg, 0.75 mmol, 77%. Recrystallization from absolute ether gave clear

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crystals: mp 62–65 °C; $[\alpha]^{25}_D$ −104.5° (c 1.00, $CHCl_3$); IR ($CHCl_3$) 3665, 3032, 3015, 3009, 2925, 2857, 1955, 1880, 1810, 1603, 1556, 1537, 1494, 1453, 1368, 1307, 1281, 1223, 1180, 1151, 1127, 1092, 1051, 1025, 996, 967, 911, 858, 824, 700, 670, 667, 649 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.58 (1, q), 0.78–1.10 (2, m), 1.14–1.50 (3, m), 1.60–1.70 (3, m), 2.08–2.20 (3, m), 4.54 (1, d), 4.75 (1, d), and 7.18–7.40 (10, m); ^{13}C NMR ($CDCl_3$) δ 9.7 (CH_2), 14.8 (CH), 24.1 (CH), 24.4 (CH_2), 28.0 (CH_2), 29.5 (CH_2), 41.2 (CH_2), 84.0 (CH), 85.3 (CH), 111.0 (C), 126.6 (CH), 126.7 (CH), 127.0 (CH), 128.0 (CH), 128.1 (CH), 128.2 (CH), 128.3 (CH), 136.7 (C), and 136.8 (C); mass spectrum (70 eV), m/z (relative intensity) 252 (3), 251 (16), 215 (15), 214 (89), 180 (31), 179 (39), 178 (16), 168 (11), 167 (52), 165 (19), 108 (14), 107 (17), 105 (36), 104 (13), 93 (72), 91 (41), 82 (13), 81 (15), 80 (98), 79 (100), 98 (14), 77 (41); exact mass calcd for $C_{15}H_{18}O$ ($M^+ - C_6H_5CHO$) 214.1358, obsd 214.1354.

2,3,5,6,7,8-Hexahydro-1*H*,4*H*-azulen-1-one (*S*,*S*)-Hydrobenzoin Ketal (7). From 2,3,5,6,7,8-hexahydro-1*H*,4*H*-azulen-1-one (1.148 g, 7.65 mmol), (*S*,*S*)-hydrobenzoin (1.091 g, 5.10 mmol), and pyridinium *p*-toluenesulfonate (100 mg, 0.40 mmol) product **7** was obtained as a very viscous pale yellow oil. Upon standing for 96 h this oil solidified: mp 46–51 °C; $[\alpha]^{25}_D$ −39.7° (c 1.74, $CHCl_3$); yield 850 mg, 2.46 mmol, 48%; IR ($CHCl_3$) 3065, 3033, 3022, 3015, 3009, 2923, 2335, 1949, 1880, 1806, 1730, 1677, 1650, 1603, 1495, 1453, 1360, 1311, 1282, 1259, 1157, 1120, 1091, 1036, 1024, 988, 938, 914, 866, 824, 700, 669, 650 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.5–1.86 (6, m), 2.08–2.26 (2, t), 2.27–2.48 (6, m), 4.66 (1, d), 4.80 (1, d), and 7.18–7.38 (10, m); ^{13}C NMR ($CDCl_3$) δ 25.2 (CH_2), 26.8 (CH_2), 27.7 (CH_2), 31.0 (CH_2), 31.3 (CH_2), 34.0 (CH_2), 36.4 (CH_2), 84.8 (CH), 86.4 (CH), 122.8 (CH), 126.4 (CH), 126.7 (CH), 127.6 (CH), 127.9 (CH), 128.2 (CH), 136.2 (C), 136.7 (C), 137.5 (C), and 146.9 (CH); mass spectrum (70 eV), m/z (relative intensity) 241 (5), 240 (29), 180 (11), 179 (9), 178 (5), 167 (21), 165 (11), 150 (18), 149 (100), 148 (17), 122 (11), 107 (14), 105 (14), 91 (33); exact mass calcd for $C_{17}H_{20}O$ ($M^+ - C_6H_5CHO$) 240.1515, obsd 240.1517.

(3a*S*,8a*R*)-2,3,5,6,7,8-Hexahydro-3a,8a-methano-1*H*,4*H*-azulen-1-one (*S*,*S*)-Hydrobenzoin Ketal (8). Cyclopropanation of ene ketal **7** (333 mg, 0.962 mmol) gave **8** as a viscous oil: $[\alpha]^{25}_D$ −46.8° (c 0.60, $CHCl_3$); yield: 214 mg, 0.595 mmol, 62%; IR ($CHCl_3$) 3064, 3030, 3019, 3011, 2921, 2860, 1945, 1880, 1800, 1494, 1453, 1361, 1331, 1311, 1276, 1236, 1194, 1174, 1153, 1130, 1107, 1091, 1074, 1049, 1024, 977, 951, 915, 868, 699, 670, 668, 650 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.76 (2, s), 1.28–1.98 (12, m), 2.35–2.52 (2, t), 4.70 (2, dd), 7.10–7.18 (2, m), and 7.24–7.35 (8, m); ^{13}C NMR ($CDCl_3$) δ 15.5 (CH_2), 26.3 (CH_2), 27.3 (CH_2), 27.6 (CH_2), 30.5 (C), 32.2 (CH_2), 32.5 (CH_2), 33.3 (C), 33.9 (CH_2), 36.0 (CH_2), 85.1 (CH), 85.8 (CH), 121.6 (C), 126.3 (CH), 127.0 (CH), 127.8 (CH), 128.1 (CH), 128.3 (CH), 136.1 (C), and 137.6 (C); mass spectrum (70 eV), m/z (relative intensity) 255 (10), 254 (45), 180 (41), 179 (19), 167 (24), 165 (16), 164 (17), 163 (35), 148 (15), 122 (24), 121 (14), 107 (22), 106 (17), 105 (100), 94 (11), 92 (22), 91 (53); exact mass calcd for $C_{18}H_{22}O$ ($M^+ - C_6H_5CHO$) 254.1671, obsd 254.1675.

(+)-Norcaranone (9). To a solution of recrystallized bicyclo[4.1.0]heptan-2-one (*S*,*S*)-hydrobenzoin ketal (**4**) (278 mg, 0.91 mmol) in methanol (10 mL) at room temperature was added 2.7 M aqueous HCl (1.0 mL). Progress of the reaction was monitored by TLC (20% ethyl acetate/hexanes). After 1.5 h the mixture was poured into saturated aqueous sodium bicarbonate (30 mL) and extracted with pentane (3 × 50 mL) and anhydrous diethyl ether (3 × 50 mL). The combined ether/pentane extracts were dried ($MgSO_4$), filtered, and concentrated by atmospheric distillation. Chromatography on silica gel 60 (75 g) eluted with 20% ether/pentane and removal of the volatiles by atmospheric distillation gave (+)-norcaranone (**9**) mixed with a small amount of ether/pentane. Yield corrected for solvents (by ^1H NMR): 75.3 mg, 68.5 mmol, 75.3%; $[\alpha]^{25}_D$ +15.6° (c 3.7, $CHCl_3$) [lit.[13a] $[\alpha]^{25}_D$ +15.3° (c 1.28, $CHCl_3$)]. (*S*,*S*)-Hydrobenzoin was also recovered in 90% yield.

Registry No. **1**, 117583-49-0; **2a**, 117583-50-3; **2b**, 117676-99-0; **3**, 117583-51-4; **4a**, 117583-52-5; **4b**, 117677-00-6; **5**, 117583-53-6; **6a**, 117583-54-7; **6b**, 117677-01-7; **7**, 117583-55-8; **8a**, 117583-56-9; **8b**, 117677-02-8; **9**, 82334-95-0; 2-cyclopenten-1-one, 930-30-3; (*S*,*S*)-hydrobenzoin, 2325-10-2; 2-cyclohexen-1-one, 930-68-7; 2-cyclohepten-1-one, 1121-66-0; 2,3,5,6,7,8-hexahydro-1*H*,4*H*-azulen-1-one, 769-32-4.

Facile Oxidation of Manganese(II) to Manganese(III) in Long Chain Carboxylic Acids

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Manganese compounds have commonly been used as oxidizing agents and catalysts in organic reactions.[1] Occasionally, it is difficult to find a suitable manganese compound that is also soluble in the appropriate reaction medium. In this connection, during the preparation of manganese(II) nonanoate, we observed an interesting series of reactions that lead to facile formation of Mn(III) from Mn(II) when manganese(II) acetate tetrahydrate is heated with long chain fatty acids.

Manganese(II) acetate tetrahydrate dissolves in nonanoic acid at room temperature after about 30 min of stirring, giving a cloudy mixture that gradually yields a white, gelatinous mass. This gel is evidently the solvated Mn(II) salt of nonanoic acid. If this mixture is then heated to 95 °C in air, the gel dissolves, and the solution gradually turns deep reddish brown. If the solution is purged with nitrogen at 95 °C, the red-brown color is gradually expelled and the mixture becomes water-white. The development and discharge of color by sparging with air or nitrogen at 95 °C is quite reversible over many cycles.

If the mixture in its colorless state (under nitrogen) is cooled to room temperature, a white, gelatinous mass of manganese(II) nonanoate precipitates from the solution as described above. If the mixture is brought to the red-brown state with air and cooled, the material stays clear for several days but then slowly precipitates white gel on further standing.

The change of color of manganese nonanoate to red-brown with air and water-white with nitrogen reflects a facile redox cycle, and indeed, a visible spectrum of the colored solution (maxima at 458 and 495 nm) is almost identical with that reported by Kochi[2] for mixtures of Mn(III) with Mn(II) (maxima at 462 and 494 nm). It can be estimated from quantitative spectrophotometry that in 30 min approximately 37% of the manganese in a 0.059 M solution of manganese(II) acetate tetrahydrate is oxidized to Mn(III) in air-sparged nonanoic acid at 95 °C (corresponding to an estimated rate of 1.2×10^5 mol/L/s). However, Mn(II) is not easily oxidized to Mn(III) by molecular oxygen except under very alkaline conditions,[3] which certainly did not prevail in our system.

A likely reaction mechanism for the formation of significant quantities of Mn(III) from Mn(II) in nonanoic acid is as follows. An initial trace of Mn(III) is formed by reaction of Mn(II) salt with small amounts of hydroperoxide[4] (eq 1) present in the nonanoic acid from aut-

$$ROOH + Mn(II) \rightarrow RO^{\bullet} + OH^- + Mn(III) \quad (1)$$

oxidation (the acid was found to contain 9.6×10^{-4} M active oxygen, a value that rose to 1.8×10^{-3} M after heating to 100 °C for 2 h). This initial trace of Mn(III) oxidatively decarboxylates the nonanoic acid according to

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