Epoxidation of Fluorinated Diene 8. A solution of 9.5 g (70 mmol) of 8[8] in 30 mL of CH_2Cl_2 was added to 200 mmol of the oxidizing reagent. After 2 min at 0 °C the reaction was worked up as described above. After the solvent was removed by distillation, the residual oil was fractionated to give the monoepoxide 9 (60%): bp (30 mm) 58 °C; IR (KBr) 1200, 1300 cm^{-1}; ^1H NMR (CD_2Cl_2) δ 2.8–2.95 (2 H, dm), 3.31 (1 H, m), 1.9–2.67 (4 H, m); ^{19}F NMR (CD_2Cl_2) δ −100.8 to −102.9 (1 F, four m), −114.5 to −117.7 (1 F, four m), −166.9 to −169.3 (1 F, two m); MS m/z 151 [(M − 1)$^+$]; calcd mass for $C_6H_7F_3O$ 151.0371, found 151.0367. Anal. Calcd for $C_6H_7F_3O$: C, 47.37; H, 4.61; F, 37.50. Found: C, 47.35; H, 4.61; F, 37.86. In this case the only effect of lowering the ratio of the oxidizer/reactant as well as the temperature was to lower the conversion of the starting material from 100 to 70%.

Epoxidation of Fluorinated Diene 10. Olefin 10[8] (9.7 g, 60 mmol) dissolved in CH_2Cl_2 (30 mL) was cooled to −40 °C and added to the oxidizing solution (160 mmol) also cooled to −40 °C. After 2 min the reaction was worked up as described above to afford the mono epoxide 12 (50%): bp (7 mm) 50–59 °C; ^1H NMR (CD_2Cl_2) δ 2.95 (1 H, m), 2.78 (1 H, t, J = 4 Hz), 2.49 (1 H, q, J = 6 Hz, 4 Hz) 1.4–2.4 (8 H, m); ^{19}F NMR (CD_2Cl_2) δ −106 (1 F, m), −125.4 (1 F, m), −175 ppm (1 F, m); MS m/z 180 (M^+), 108 [(CF_2=$CFCH_2CH_2$ − 1)$^+$], 95 [(CF_2=$CFCH_2$)$^+$]. Anal. Calcd for $C_8H_{11}F_3O$: C, 53.33; H, 6.11; F, 31.67. Found: C, 53.27; H, 6.13; F, 31.02.

Epoxidation of Fluorinated Diene 11. A solution of 5 g (26 mmol) of the olefin[8] dissolved in 20 mL of CH_2Cl_2 was added at −10 °C to 65 mmol of the oxidizing reagent. After 10 min the reaction was worked up as before to give 19% recovered starting materal and 55% monoepoxide 13: ^1H NMR (CD_2Cl_2) δ 2.95 (1 H, m), 2.78 (1 H, t, J = 4 Hz), 2.46 (1 H, q, J = 6 Hz, 4 Hz) 1.3–2.4 (12 H, m); ^{19}F NMR (CD_2Cl_2) δ −106.5 (1 F, m), −125.7 (1 F, m), −175.1 (1 F, m); MS m/z 207 [(M − 1)$^+$]; calcd mass for $C_{10}H_{14}F_3O$ 207.0997, found 207.1029; 95 [(CF_2=$CFCH_2$)$^+$].

Epoxidation of Pentafluorophenylethylene (14). A solution of 8 g of 14[18] in 20 mL of CH_2Cl_2 was added to the reagent solution (100 mmol in 440 mL of 10:1 CH_3CN–H_2O). After 5 min the reaction was neutralized with solid sodium bicarbonate. Most of the liquid was distilled off under reduced pressure (80 mm). The remaining liquid (50 mL) was poured into water, extracted with $CFCl_3$, and worked up as usual to give 6.7 g (85% yield) of epoxide 15:[10] bp 34–37 °C (0.1 mm); ^1H NMR (CD_2Cl_2) δ 3.2 (2 H, 2 m), 4.0 (1 H, m); ^{19}F NMR (CD_2Cl_2) δ −143.9 (2 F, m), −154.1 (1 F, t, J = 21 Hz), −162.5 (2 F, m); MS m/z 210 (M^+).

Epoxidation of a Mixture of 3-(Perfluoroalkyl)-1-propenes (17).[12] To a solution of 100 mmol of the oxidizing reagent in 440 mL of CH_3CN–H_2O (10:1) was added 20 g of a 1:1:1 mixture of $C_6F_{13}CH_2CH$=CH_2/$C_8F_{17}CH_2CH$=CH_2/$C_{10}F_{21}CH_2CH$=CH_2 in 50 mL of CH_2Cl_2. After 10 min the reaction was neutralized with solid sodium bicarbonate. The reaction mixture was poured into water, extracted with $CFCl_3$, and worked up as usual. The crude product (16.3 g) was shown to be a 1:1:1 mixture of epoxides 18: MS (R_f = C_6F_{13}) m/z 360 (M^+), (R_f = C_8F_{17}) m/e 460 (M^+), (R_f = $C_{10}F_{21}$) m/e 560 (M^+).

A Convenient Synthesis of γ-Hydroxy α,β-Unsaturated Sulfones

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The synthetic versatility offered by γ-hydroxy α,β-unsaturated sulfones, especially as acceptors in our [3 + 2] cycloadditions, induced us to explore more convenient syntheses.[1-3] Extension of the excellent method of Tanikaga for the synthesis of γ-hydroxy α,β-unsaturated esters, which employs a Knoevenagel condensation in tandem with an allylic sulfoxide–sulfenate rearrangement,[4] to sulfones is highly attractive.[5-7] A recent communication, employing (phenylsulfinyl)(phenylsulfonyl)methanes,[8] leads us to give a full account of our work in this area.

Scheme I.[a] Synthesis of ((4-Chlorophenyl)sulfinyl)(phenylsulfonyl)methane

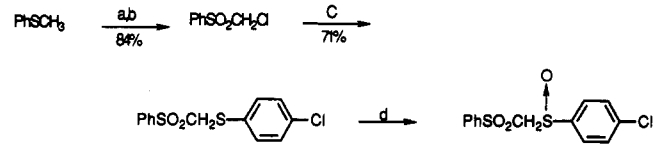
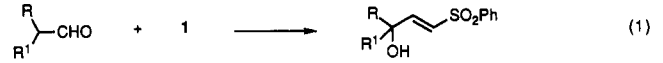


Table I. Synthesis of γ-Hydroxy α,β-Unsaturated Sulfones

entry	R	R′	temp, °C	time, h	% yield
1	H	H	rt	–	–
2	CH_3	H	rt	2	53
3	CH_3	CH_3	62–80	16	41
4	TBDMSO$(CH_2)_4$	H	rt	1	66
5	$CH_3(CH_2)_3$	H	rt	2	79
6	CH_2=$CH(CH_2)_7$	H	rt	2	90
7	$(CH_3)_2C$=$CHCH_2CH_2CH(CH_3)$	H	rt	2	94[a]
8	$PhCH(CH_3)$	H	rt	2	94[b]
9	Ph	H	rt	–	–
10	$(CH_3)_3CCH_2CH(CH_3)$	H	rt	2	93[c]

[a] dr 1:1. [b] dr 1.2:1. [c] dr 1.4:1.

We chose to employ ((4-chlorophenyl)sulfinyl)(phenylsulfonyl)methane (1) as our preferred reagent. Scheme I outlines its synthesis in 47% overall yield from thioanisole (MCPBA = *m*-chloroperoxybenzoic acid). Condensations with aldehydes according to eq 1 and Table I were normally performed by allowing an acetonitrile solution of equivalent quantities of reactants to stir with 1 equiv of piperidine at room temperature. The products show



(1)

characteristic infrared absorbances at approximately 3600 cm^{-1} for the hydroxyl group and 1350–1150 cm^{-1} for the sulfone groups. ^1H NMR coupling constants for the vinyl hydrogens indicate only the *E* isomers are obtained in every case.

The reaction is relatively insensitive to the presence of water or impurities, so that anhydrous solvents or inert atmosphere conditions are not required. Substitution of the aldehyde at the α-position required higher temperatures and resulted in somewhat lower yield (Table I, entry 3), but β-substitution was not deleterious (Table I, entries 7, 8, and 10). The reaction failed with acetaldehyde and phenylacetaldehyde, possibly due to preferential self-condensation reactions.

Condensation of β-alkyl-substituted aldehydes (Table I, entries 7, 8, and 10) gave essentially nonselective mixtures of diastereomers. On the other hand, reaction of 1 with the carbohydrate-derived aldehyde 3 (prepared from 2 by the method of Nicolaou)[9] gave sulfone 5 as a 7.6:1

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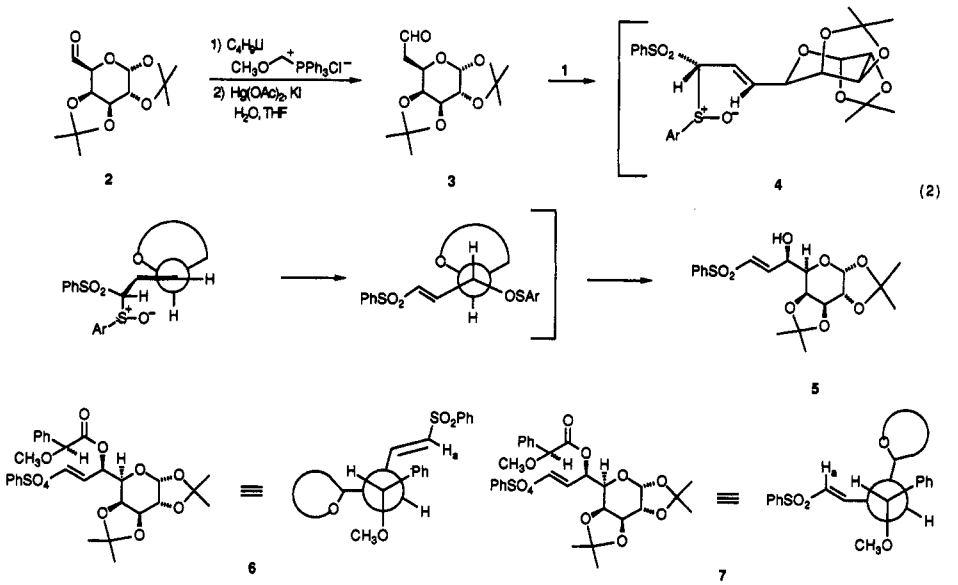
Table II. Experimental Details

entry	R(R')CHCHO, R (wt, mmol)	R'	1 wt, mmol	piperidine wt, mmol	CH_3CN, mL	time, h	product wt, % yield	mp, °C
1	CH_3 (103.4 mg, 1.7)	H	546 mg, 1.74	151.6 mg, 1.78	3.5 + 5.0	2	179 mg, 53[a]	54–5
2	CH_3 (259 mg, 3.6)	CH_3	1.0 g, 3.2	307 mg, 3.6	3 + 9	12 + 4[b]	294 mg, 41[c]	102–3
3	TBDMSO $(CH_2)_4$	H	see text					
4	$CH_3(CH_2)_3$ (200.3 mg, 2.0)	H	500 mg, 1.6	170.3 mg, 2.0	2 + 4	2	321 mg, 79[d]	63
5	CH_2=$CH(CH_2)_7$ (403.9 mg, 2.4)	H	500, mg, 1.6	204 mg, 2.4	2 + 4	2	465 mg, 90[e]	49–50
6	$(CH_3)C$=$CHCH_2CH(CH_3)$ (370 mg, 2.4)	H	500 mg, 1.6	204, mg, 2.4	2 + 4	2	493 mg, 94[e]	oil
7	$PhCH(CH_3)$ (356 mg, 2.4)	H	500 mg, 1.6	204 mg, 2.4	2 + 4	2	450 mg, 94[a]	nd[f]
8	$(CH_3)_3CCH_2CH(CH_3)$ (34.4 mg, 2.4)	H	500 mg, 1.6	204 mg, 2.4	2 + 4	2	439 mg, 93[e]	nd[f]
9	3 (100 mg, 0.37)		142 mg, 0.45	38.3 mg, 0.45	0.5 + 1.5	2	115 mg, 73[a]	foam

[a] Chromatographic solvent 2:1 hexane–ethyl acetate. [b] 62 °C and then reflux. [c] Chromatographic solvent 5:5:3 hexane–methylene chloride–ether. [d] Chromatographic solvent 3:1 hexane–ethyl acetate. [e] Chromatographic solvent 1:1 hexane–ether. [f] Mp not determined since product is a diastereomeric mixture.

Scheme II



mixture of diastereomers in 73% yield (Scheme II). The absolute stereochemistry of the prevailing isomer has been assigned as 6*R* based upon conversion of the mixture to the (*S*)-*O*-methyl mandelate esters. The upfield shift (δ 5.84) experienced by H_a in the major isomer 6 compared to the minor isomer 7 (δ 6.27) arises from shielding of this proton by the phenyl substituent as revealed in the extended-Newman projections depicted. This stereochemical outcome can be rationalized by invoking a transition-state conformer in which the bulky pyranose ring is oriented such that nonbonded interactions with the aryl sulfoxide as well as torsional interactions with the olefin are minimized as depicted in Scheme II.

As indicated by the previous discussion, the mild reaction conditions employed in this condensation are tolerant of a range of functionality including silyl ethers, acetals, and olefins. The high diastereoselectivity demonstrated for the condensation of β-heteroatom-substituted aldehydes and the possibility of asymmetric induction through the use of enantiomerically pure sulfoxides[11] are promising areas for further development. The rapid construction of γ-hydroxy α,β-unsaturated sulfones, made possible by the methodology described herein, should greatly enhance their viability as reaction partners for stereoselective organic synthesis.

Experimental Section

((4-Chlorophenyl)thio)methyl Phenyl Sulfone. A solution of SO_2Cl_2 (22.5 g, 13.5 mL, 167 mmol) in 40 mL of CH_2Cl_2 was added dropwise to a solution of thioanisole (21.0 g, 20 mL, 169 mmol) in 125 mL of CH_2Cl_2 at reflux. After 2 h at that temperature, the mixture was cooled and the solvent was removed in vacuo. A portion of the resulting crude chloromethyl phenyl sulfide (16.5 g, 104 mmol) in 400 mL of methanol at 0 °C was treated with a solution of oxone[12] (128 g, 208 mmol) in 530 mL of water at rt for 48 h. After being partitioned between water and CH_2Cl_2, the combined organic layers were washed with 500 mL of saturated aqueous sodium chloride, dried ($MgSO_4$), and filtered, and the solvents were removed in vacuo. The remaining

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colorless liquid crystallized from cold ether–hexane and was recrystallized (ether–hexane, trace CH_2Cl_2) to give 16.7 g (84%) of chloromethyl phenyl sulfone[13] as colorless prisms. ^1H NMR (200 MHz, $CDCl_3$): δ 7.5–8.0 (m, 5 H), 4.50 (s, 2 H). 4-Chlorothiophenol (4.6 g, 32 mmol) in 15 mL of ethanol, followed by the above chloride (5.0 g, 26 mmol) in 10 mL of ethanol was added to a solution of sodium ethoxide (from 760 mg of Na, 32 mg-atom) in 25 mL of absolute ethanol. After heating at reflux for 24 h, the mixture was cooled, diluted with 100 mL of 10% aqueous NaOH, and extracted with methylene chloride. The organic extracts were dried ($MgSO_4$) and filtered, and the solvent was removed in vacuo. The residue crystallized from hexane–ether and was recrystallized from 95% ethanol to give 5.53 g (71%) of the titled compound as a white solid, mp 79 °C (lit.[14] mp 67–69 °C). ^1H NMR (200 MHz, $CDCl_3$): δ 7.1–7.9 (m, 9 H), 4.23 (s, 2 H).

((4-Chlorophenyl)sulfinyl)(phenylsulfonyl)methane (1). MCPBA (83%, 13.4 mmol) was added slowly to a solution of the above sulfide (4.0 g, 13.4 mmol) in 80 mL of CH_2Cl_2 at 0 °C. After 15 min, the reaction was quenched with 75 μL of dimethyl sulfide and washed with 40 mL of saturated aqueous $NaHCO_3$. The organic layer was dried ($MgSO_4$) and filtered, and the solvent was removed in vacuo, leaving 3.34 g (79%) of the titled compound as a white solid, mp 107–109 °C (ether). IR ($CDCl_3$): 1580 (m), 1470 (s), 1450 (s), 1180 (s), 1150 (m), 1080 (s), 1050 (s) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 7.45–8.00 (m, 9 H), 4.38 and 4.34 (AB dd, J = 16 Hz, 2 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 141.0, 134.7, 129.9, 129.5, 128.4, 125.6, 79.6. MW: calcd for $C_{13}H_{11}{}^{34}ClO_3S_2$ (M^+) 313.9838, found 313.9843. MW: calcd for $C_{13}H_{11}{}^{36}ClO_3S_2$ (M^+) 315.9809, found 315.9803.

Representative Procedure for Preparation of γ-Hydroxy α,β-Unsaturated Sulfones. (*E*)-7-(*tert*-Butyldimethylsiloxy)-1-(phenylsulfonyl)-1-hepten-3-ol. A solution of 6-(*tert*-butyldimethylsiloxy)hexanal[15] (2.0 g, 8.7 mmol) in 10 mL of acetonitrile was added slowly to a mixture of piperidine (0.7 g, 812 μL, 8.7 mmol) and sulfoxide 1 (2.7 g, 8.7 mmol) in 30 mL of acetonitrile. After 1 h at rt, the mixture was diluted with 200 mL of ether and washed with 100 mL of water. The aqueous layer was washed with 100 mL of ether, the combined organic layers were washed with 100 mL of 10% aqueous NaOH, dried ($MgSO_4$), and filtered, and the solvent was removed in vacuo. Flash chromatography (silica gel, 2:1 hexane–ether) yielded 2.1 g (66%) of the titled compound as a clear, colorless oil which solidified to a waxy solid, mp 48–50 °C, upon standing. IR ($CDCl_3$): 3600 (w), 3480 (b), 1470 (w), 1460 (w), 1450 (w), 1150 (s), 1090 (s). ^1H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, J = 8.2 Hz, 2 H), 7.58 (t, J = 7.6 Hz, 1 H), 7.50 (t, J = 7.8 Hz, 2 H), 6.95 (dd, J = 15.1, 4.4 Hz, 1 H), 6.57 (dd, J = 15.0, 1.6 Hz, 1 H), 4.35 (m, 1 H), 3.57 (t, J = 6.0 Hz, 2 H), 2.49 (m, 1 H), 1.3–1.7 (m, 6 H), 0.85 (s, 9 H), 0.01 (s, 6 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 148.3, 140.3, 133.4, 129.5, 129.3, 127.6, 70.1, 62.9, 35.8, 32.1, 25.9, 21.7, 18.3, -5.3. MW: calcd for $C_{15}H_{23}O_4SSi$ ($M - C_4H_9$)$^+$ 327.1086, found 327.1081.

Characterization Data. (*E*)-1-(Phenylsulfonyl)-3-buten-3-ol. FTIR ($CDCl_3$): 3617 (2), 1448 (w), 1317 (m), 1308 (m), 1280 (w), 1149 (s), 1087 (w), 1025 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.87 (dd, J = 7.1, 1.4 Hz, 2 H), 7.59 (tt, J = 7.4, 1.3 Hz, 1 H), 7.53 (tm, J = 7.4 Hz, 2 H), 6.98 (dd, J = 14.9, 3.6 Hz, 1 H), 6.58 (dd, J = 14.9, 1.8 Hz, 1 H), 4.54 (m, 1 H), 1.63 (d, J = 4.9 Hz, 1 H), 1.34 (d, J = 6.7 Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 149.4, 140.2, 133.6, 129.5, 129.1, 127.7, 66.2, 22.1. Anal. Calcd for $C_{10}H_{12}O_3$: C, 56.58; H, 5.71; MW, 212.0507. Found: C, 56.69; H, 5.78; MW, 212.0519.

(*E*)-3-Methyl-1-(phenylsulfonyl)-3-buten-3-ol. FTIR ($CDCl_3$): 3600 (b, w), 1318 (m), 1285 (w), 1154 (m), 1146 (m), 1086 (w), 1018 (s) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.87 (dd, J = 7.0, 1.7 Hz, 2 H), 7.59 (t, J = 7.3 Hz, 1 H), 7.53 (tm, J = 7.5 Hz, 2 H), 6.99 (d, J = 14.9 Hz, 1 H), 6.55 (d, J = 15.0 Hz, 1 H), 1.53 (s, 1 H), 1.36 (s, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.6, 140.5, 133.6, 129.4, 128.1, 127.7, 70.8, 28.9. MW: calcd for $C_{10}H_{11}O_3S$ ($M - CH_3$)$^+$ 211.0429, found 211.0406.

(*E*)-1-(Phenylsulfonyl)-1-hepten-3-ol. FTIR ($CDCl_3$): 3600 (w), 1448 (w), 1317 (m), 1307 (m), 1191 (w), 1149 (s), 1087 (m), 1019 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.87 (m, 2 H), 7.56 (m, 3 H), 6.98 (dd, J = 5.0 Hz, 1 H), 1.5–1.7 (m, 2 H), 1.3–1.5 (m, 4 H), 0.88 (m, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 148.8, 140.5, 133.4, 129.5, 129.3, 127.5, 69.9, 35.7, 26.8, 22.0, 13.4. Anal. Calcd for $C_{13}H_{18}O_3S$: C, 61.38; H, 7.15; MW, 254.0076. Found: C, 61.55; H, 7.08; MW, 254.1000.

(*E*)-1-(Phenylsulfonyl)-1,11-dodecadien-3-ol. FTIR ($CDCl_3$): 3614 (w), 1448 (w), 1347 (m), 1308 (m), 1148 (s), 1087 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.86 (dd, J = 7.1, 1.7 Hz, 2 H), 7.60 (t, J = 7.4 Hz, 1 H), 7.52 (t, J = 7.6 Hz, 2 H), 6.97 (dd, J = 14.9, 3.8 Hz, 1 H), 6.57 (dd, J = 14.9, 1.8 Hz, 1 H), 5.78 (ddt, J = 17.0, 10.3, 6.6 Hz, 1 H), 4.97 (dm, J = 17.1 Hz, 1 H), 4.91 (dm, J = 10.3 Hz, 1 H), 4.34 (m, 1 H), 2.00 (q, J = 7.0 Hz, 2 H), 1.82 (d, J = 4.9 Hz, 1 H), 1.4–2.7 (m, 2 H), 1.2–1.4 (m, 10 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 148.9, 140.5, 139.1, 133.4, 129.5, 129.3, 127.6, 114.2, 69.9, 36.0, 33.4, 28.9 (2), 28.6, 28.5, 24.7. MW: calcd for $C_{18}H_{24}O_2S$ ($M - H_2O$)$^+$ 304.1497, found 304.1478.

(*E*)-4,8-Dimethyl-1-(phenylsulfonyl)-1,7-nonadien-3-ol. FTIR ($CDCl_3$): 3680 (w), 3600 (w), 1448 (w), 1317 (m), 1308 (m), 1149 (s), 1087 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.86 (dd, J = 7.0, 1.6 Hz, 2 H), 7.60 (t, J = 7.4 Hz, 1 H), 7.51 (t, J = 7.6 Hz, 2 H), 6.98 (dd, J = 15.0, 4.1 Hz, 0.5 H), 6.96 (dd, J = 15.0, 3.8 Hz, 0.5 H), 6.59 (dd, J = 14.9, 1.7 Hz, 0.5 H), 6.59 (dd, J = 15.0, 1.8 Hz, 0.5), 5.02 (m, 1 H), 4.32 (m, 0.5 H), 4.26 (m, 0.5 H), 1.8–2.1 (m, 3 H), 1.70 (m, 1 H), 1.65 (s, 3 H), 1.56 (s, 3 H), 1.3–1.5 (m, 1 H), 1.0–1.3 (m, 1 H), 0.88 (d, J = 6.8 Hz, 1.5 H), 0.82 (d, J = 7.0 Hz, 1.5 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 148.0, 147.2, 140.8, 133.4, 132.0, 130.9, 130.5, 129.3, 127.6, 124.0, 74.09, 73.3, 38.2, 37.6, 32.6, 31.8, 25.3, 25.2 (2), 17.3, 14.7, 13.6. MW: calcd for $C_{17}H_{24}O_3S$ (M^+) 308.1446, found 308.1426.

(*E*)-4-Phenyl-1-(phenylsulfonyl)-1-penten-3-ol. FTIR ($CDCl_3$): 3580 (w), 1448 (w), 1317 (m), 1308 (m), 1148 (s), 1087 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.79 (d, J = 7.9 Hz, 2 H), 7.57 (m, 1 H), 7.50 (m 2 H), 7.1–7.4 (m, 5 H), 7.04 (dd, J - 14.9, 1.9 Hz, 0.5 H), 6.92 (dd, J = 14.7, 3.8 Hz, 0.5 H), 6.52 (dd, J = 14.9, 1.9 Hz, 0.5 H), 6.50 (dd, J = 14.9, 1.7 Hz, 0.5 H), 4.43 (m, 1 H), 2.98 (p, J = 6.9 Hz, 0.5 H), 2.92 (p, J = 6.9 Hz, 0.5 H), 1.72 (m, 1 H), 1.32 (d, J = 7.1 Hz, 1.5 H), 1.28 (d, J = 7.1 Hz, 1.5 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.1, 146.6, 142.2, 141.5, 140.6, 133.4, 131.0, 130.9, 129.3, 128.8, 128.0, 127.9, 127.6, 127.6, 127.2 (2), 74.5, 74.4, 45.6, 45.2, 16.5, 15.5. MW: calcd for $C_{17}H_{17}O_2S$ ($M - OH$)$^+$ 285.0949, found: 285.0935.

(*E*)-1-(Phenylsulfonyl)-4,6,6-trimethyl-1-hepten-3-ol. FTIR ($CDCl_3$): 3615 (w), 1477 (w), 1448 (w), 1367 (w), 1318 (m), 1308 (m), 1148 (s), 1087 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$); δ 7.87 (d, J = 7.8 Hz, 2 H), 7.60 (t, J = 7.1 Hz, 1 H), 7.52 (t, J = 7.5 Hz, 2 H), 6.98 (dd, J = 14.9, 3.5 Hz, 0.4 H), 6.94 (dd, J = 15.0, 3.5 Hz, 0.6 H), 6.61 (dd, J = 14.9, 1.9 Hz, 0.6 H), 6.59 (dd, J = 14.9, 1.9 Hz, 0.4 H), 4.24 (m, 1 H), 1.76 (m, 1 H), 1.66 (m, 1 H), 1.31 (m, 1 H), 0.95 (d, J - 6.9 Hz, 1.8 H), 0.90 (m, 1 H), 0.89 (d, J = 7.0 Hz, 1.2 H), 0.87 (s, 3.6 H), 0.85 (s, 5.4 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 148.0, 147.6, 140.5, 133.2, 130.6, 130.3, 129.1, 127.3, 74.8, 74.4, 46.1, 45.1, 34.6, 34.4, 30.3 (2), 29.3, 17.8, 16.6. MW: calcd for $C_{13}H_{13}O_3S$ ($M - C_5H_{11}$)$^+$ 225.0585, found 225.0565.

(*E*)-6-(2-(Phenylsulfonyl)vinyl)-α-D-galactose (5). FTIR ($CDCl_3$): 3650 (w), 3510 (w), 1318 (m), 1309 (m), 1165 (m), 1149 (s), 1087 (m), 1070 (s), 1010 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) major isomer: δ 7.86 (dd, J = 7.2, 1.4 Hz, 2 H), 7.58 (m, 1 H), 7.49 (m, 2 H), 7.17 (dd, J = 15.0, 3.2 Hz, 1 H), 6.72 (dd, J = 15.1, 2.0 Hz, 1 H), 5.51 (d, J = 5.0 Hz, 1 H), 4.59 (dd, J = 17.9, 2.5 Hz, 1 H), 4.55 (m, 1 H), 4.32 (dd, J = 10.2, 1.9 Hz, 1 H), 4.30 (dd, J = 5.0, 3.5 Hz, 1 H), 3.69 (dd, J = 7.0, 1.8 Hz, 1 H), 3.04 (d, J = 6.6 Hz, 1 H), 1.43 (s, 3 H), 1.41 (s, 3 H), 1.29 (s, 6 H). Minor isomer, partial: δ 7.04 (dd, J = 14.5, 3.2 Hz, 1 H), 6.78 (m, 1 H), 4.24 (m, 1 H), 3.56 (m, 1 H). ^{13}C NMR (7m MHz, $CDCl_3$) major isomer: δ 146.3, 140.9, 133.3, 131.2, 129.3, 127.8, 109.9, 108.9, 96.4, 77.4, 70.8, 70.4, 69.5, 69.4, 25.7, 25.6, 24.6, 24.2. Minor isomer, partial: δ 133.5, 129.3, 96.3, 24.0. MW: calcd for $C_{19}H_{23}O_8S$ ($M - CH_3$)$^+$ 411.1113, found 411.1130.

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Supplementary Material Available: ^1H and ^{13}C NMR spectra for each entry of Table I and for 3 and 5 (22 pages). Ordering information is given on any current masthead page.

Solid Superacid Catalyzed Organic Synthesis. 6.[1] Perfluorinated Resinsufonic Acid (Nafion-H) Catalyzed Ring Closure Reaction of 2,2'-Dihydroxybiphenyls. A Preparative Route to Dibenzofurans

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Introduction

The acid-catalyzed ring closure of 2,2'-dihydroxybiphenyls to corresponding dibenzofurans has been studied using various acid catalysts.[2-4] However, these methods require elevated temperatures (>350 °C), long reaction times, and an excess of protic and Lewis acids. Furthermore, some of these reactions were plagued with undesirable side products during cyclization.[4] Therefore, the scope and selectivity for the preparation of dibenzofuran derivatives have been limited.

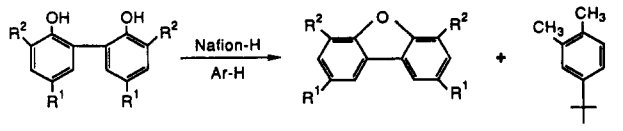
Now we wish to report an efficient and mild procedure for the ring closure of 2,2'-dihydroxybiphenyls in the presence of the solid superacid, Nafion-H (a solid perfluorinated resinsulfonic acid) to afford dibenzofuran derivatives in good to moderate yields.

Results and Discussion

The preparative route for 2,2'-dihydroxy-3,3'-dimethyldiphenyl (**1b**) is shown in Scheme I, and the preparation of other dihydroxybiaryls **1a**, **1d**, and **1e** using the *tert*-butyl group as a positional protective group[5] was described in a previous paper. Compound **1c** was prepared according to the literature.[6]

The attempted ring closure reaction of 2,2'-dihydroxybiphenyl (**1a**), carried out under benzene reflux for 36 h in the presence of Nafion-H, only led to recovery of starting material. However, under toluene or *o*-xylene reflux the desired dibenzofuran **2a** was obtained (see Table I). In the case of toluene reflux, it takes more than 36 h to complete the reaction, but under *o*-xylene reflux only 12 h are required. Products (**2**) were simply isolated by filtration of the hot reaction mixture and evaporation of the solvent. The reactions are very clean, with water the only byproduct formed during the reaction. Optimum yield of dibenzofuran **2** was obtained with 50% of the catalyst, whereas 30% gave only slightly lower yield.

The Nafion-H-catalyzed ring closure was further applied to the methyl-substituted 2,2'-dihydroxybiphenyls **1b** and **1c** to afford 4,6-dimethyl- (**2b**) and 2,8-dimethyldibenzofuran (**2c**) in 40% and 90% yield, respectively. However,



1 **2** **10**

a : $R^1 = R^2 = H$
b : $R^1 = H$, $R^2 = Me$
c : $R^1 = Me$, $R^2 = H$
d : R^1 = t-Bu, $R^2 = H$
e : $R^1 = R^2$ = t-Bu

in the case of *tert*-butyl-substituted 2,2'-dihydroxybiphenyls **1d** and **1e**, it was found that the trans-*tert*-butylation occured along with the ring closure reaction to afford mixture of **2a** and 2,8-di-*tert*-butyldibenzofuran (**2d**).

From the above results, it might be assumed that the compound **2d** would be intermediate for the formation of **2a** from **1d** and **1e** under the condition used. Although attempts to separate these reaction products failed by chromatography, further treatment of the reaction mixture with excess Nafion-H catalyst (100 wt %) carried out under *o*-xylene reflux for 24 h did not result in complete removal of *tert*-butyl groups. Again mixtures were obtained.

Based on the above results, one might conclude that initially de-*tert*-butylation occurs to give 2,2'-dihydroxybiphenyl **1a** from **1d** and/or **1e** and followed by cyclization of **1a** to afford compound **2a**. However, formation of compound **2d** indicates direct ring closure of **1d**.

It has been previously reported by us[7] that treatment of 3,3',5,5'-tetra-*tert*-butyl-2,2'-dihydroxybiphenyl (**1e**) in the presence of Nafion-H under toluene reflux gives trans-*tert*-butylated product, 2,2'-dihydroxybiphenyl, in high yield without the formation of dibenzofuran.

Utilizing this reaction we have developed a one-pot procedure to convert di-*tert*-butyl-2,2'-dihydroxybiphenyls **1d** and 8 directly to dibenzofurans **2a** and **2b** much more conveniently. Thus, heating of compounds **1a** and 8 with Nafion-H catalyst in *o*-xylene at 120 °C for 2 h followed by heating at *o*-xylene reflux gives the desired dibenzofurans **2a** and **2b** in 98% and 50% yield, respectively.

It was also found that this ring closure reaction was also applicable to the corresponding 2,2'-dimethoxybiphenyls under mild reaction conditions. When 5,5'-dimethyl-2,2'-dimethoxybiphenyl (**12**) was treated in refluxing *o*-xylene for 36 h in the presence of Nafion-H (50 wt %), the desired product **2c** was obtained in 60% yield. In this reaction, intermediate formation of 5,5'-dimethyl-2,2'-dihydroxybiphenyl (**1c**) was observed only by GLC analysis without isolation.

The present method provides excellent yields, easy isolation of the products, and ready regeneration of the catalyst without the loss of catalytic activity.

Experimental Section

All melting and boiling points are uncorrected. NMR spectra were recorded at 270 MHz with a Nippon Denshi JEOL FT-270 NMR spectrometer with Me_4Si as an internal reference. IR

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