of concentrated HCl). The reaction mixture was next extracted with ether. The ether extract was washed with water, dried (Na_2SO_4), and evaporated to yield 2-(diphenylphosphinyl)-1-naphthol (**4a**) as a white solid. The yield of **4a** after crystallization from methylene chloride/hexanes was 2.7 g (52%), mp 167 °C: ^{31}P NMR δ + 40.6; ^1H NMR δ 6.85–7.90 (m, 15 H, Ar), 8.35–8.50 (m, 1 H, Ar), 12.30 (b, 1 H, OH); ^{13}C NMR δ 102.6 (d, 106.9 Hz, C_2), 119.1 (d, 12.6 Hz, C_4), 123.8, 126.2 (d, 9 Hz, C_{8a}), 126.4, 126.6 (d, 10.6 Hz, C_3), 127.8, 129.2 (d, 12.4 Hz, $C_{3'}$), 129.4, 132.5 (d, 105.3 Hz, $C_{1'}$), 132.5 (d, 10.4 Hz, $C_{2'}$), 133.0 (d, 2.9 Hz, $C_{4'}$), 136.9 (C_{4a}), 163.3 (d, 2.9 Hz, C_1).

Anal. Calcd for $C_{22}H_{17}O_2P$: C, 76.74; H, 4.94; P, 9.01. Found: C, 76.43; H, 4.92; P, 9.06.

Bis(1-hydroxy-2-naphthyl)phenylphosphine Oxide (4b). *n*-Butyllithium (21.68 mL, 2.5 M) was added to a solution of diisopropylamine (5.47 g, 54.2 mmol) in dry THF (35 mL) at −78 °C under an argon atmosphere. After 30 min, a solution of di(1-naphthyl) phenylphosphinate[18] (**3b**) (5.55 g, 13.5 mmol) in dry THF (35 mL) was added. After being stirred at −78 °C for 1 h, the reaction mixture was warmed to room temperature. After 2 h, the reaction mixture was added to dilute HCl (85 mL of water added to 15 mL of concentrated HCl). The reaction mixture was extracted with ether (150 mL). The ether extract was washed with water, dried (Na_2SO_4), and evaporated to yield **4b** as a white solid. The yield of **4b** after crystallization from methylene chloride/hexanes was 3.0 g (54%), mp 182–183 °C: ^{31}P NMR δ +51.4; ^1H NMR δ 7.0–7.9 (m, 15 H, Ar), 8.3–8.5 (m, 2 H, Ar), 11.6 (s, 2 H, OH); ^{13}C NMR δ 102.7 (d, 108.3 Hz, C_2), 119.6 (d, 12.6 Hz, C_4), 123.8, 126.2 (d, 10.8 Hz, C_3), 126.7, 127.9, 129.5 (d, 13.1 Hz, $C_{3'}$), 129.7, 132.4 (d, 106.3 Hz, $C_{1'}$), 132.7 (d, 11.6 Hz, $C_{2'}$), 133.8 (d, 2.8 Hz, $C_{4'}$), 137.1, 163.0 (d, 3.0 Hz, C_1).

Anal. Calcd for $C_{26}H_{19}O_3P$: C, 76.09; H, 4.63; P, 7.56. Found: C, 76.48; H, 4.87; P, 7.60.

Tris(1-hydroxy-2-naphthyl)phosphine Oxide (4c). *n*-Butyllithium (21.68 mL, 2.5 M) was added to a solution of diisopropylamine (5.47 g, 54.2 mmol) in dry THF (35 mL) at −78 °C under an argon atmosphere. After 30 min, a solution of 1-naphthyl phosphate[19] **3c** (4.30 g, 9 mmol) in dry THF (35 mL) was added. The reaction mixture was stirred at −78 °C for 1 h and then warmed to room temperature. After 2 h, the reaction mixture was added to dilute HCl (85 mL of water added to 15 mL concentrated HCl). The reaction mixture was next extracted with ether. The ether extract was washed with water, dried (Na_2SO_4), and evaporated to yield crude **4c** as a white solid. The yield of **4c** after crystallization from ethanol was 2.8 g (65%), mp 240 °C: ^{31}P NMR δ +53.70; ^1H NMR δ 7.05–7.90 (m, 18 H, Ar), 8.35–8.50 (m, 3 H, Ar), 10.55 (b, 3 H, OH); ^{13}C NMR δ 104.3 (d, 108.7 Hz, C_2), 120.2, (d, 12.8 Hz, C_4), 123.8, 125.9, 125.9 (d, 10.6 Hz, C_3), 126.8, 128.0, 129.9, 137.3, 161.4 (d, 2.6 Hz, C_1).

Anal. Calcd for $C_{30}H_{21}O_4P$: C, 75.63; H, 4.41; P, 6.51. Found: C, 75.22; H, 4.52; P, 6.46.

Diethyl (3-Hydroxy-2-naphthyl)phosphonate (6). Starting with 14.0 g of diethyl 2-naphthyl phosphate[16] (**5**) and following the procedure as for **2**, the crude product was obtained as a thick oil. ^{31}P NMR of the crude product exhibited signals at δ 21.2 and 25.3 in 2:1 ratio. On standing, **6** separated as a solid in the thick oil. **6** was collected by filtration and crystallized from hexanes as a white solid, 5.5 g (39%), mp 114 °C: ^{31}P NMR δ +21.2; ^1H NMR δ 1.34 (t, 7 Hz, 6 H, CH_3), 4.0–4.3 (m, 4 H, CH_2), 7.26–7.36 (m, 2 H, Ar), 7.48 (app t, 8.5 Hz, 1 H), 7.72 (d, 8.5 Hz, 1 H), 7.78 (d, 8 Hz, 1 H), 8.04 (d, 16.5 Hz, 1 H), 10.0 (s, 1 H, OH); ^{13}C NMR δ 16.28 (d, 6.5 Hz, CH_3), 63.23 (d, 5.0 Hz, CH_2), 112.0 (d, 11.3 Hz, C_4), 112.9 (d, 179.4 Hz, C_2), 124.4, 127.0, 127.8 (d, 15.4 Hz, C_{8a}), 129.1, 129.2, 134.7 (d, 5.9 Hz, C_1), 138.2 (d, 2.3 Hz, C_{4a}), 157.3 (d, 7.7 Hz, C_3).

Anal. Calcd for $C_{14}H_{17}O_4P$: C, 60.00; H, 6.07; P, 11.07. Found: C, 60.41; H, 6.21; P, 11.11.

(1-Hydroxy-2-naphthyl)phosphonic Acid (7). To a mixture of diethyl (1-hydroxy-2-naphthyl)phosphonate (**2**) (2.8 g, 10 mmol), acetonitrile (20 mL), and sodium iodide (4.5 g) under nitrogen was added chlorotrimethylsilane[8a] (3.25 g). The reaction mixture was stirred at room temperature for 16 h and then at 40 °C for 1 h. It was next filtered to remove NaCl and volatiles were removed on the rotary evaporator. Chloroform (30 mL) was added to the residue when some more NaCl precipitated out. After the removal of NaCl by filtration, chloroform was removed on the rotary evaporator. Water (20 mL) was added to the crude silyl ester. After 15 min of stirring at room temperature, the aqueous layer was separated and evaporated to dryness on the rotary evaporator. Acetonitrile (25 mL) was added to the residue and the mixture was evaporated to obtain a slightly yellow solid. The solid residue was stirred for 15 min with methylene chloride (40 mL) and then collected by filtration. The yield of white solid **7** was 2.0 g (89%); ^{31}P NMR (D_2O/H_3PO_4 cap.) +16.6. The crude acid (0.5 g) was dissolved in ethanol (20 mL) and aniline (0.36 g) was added. The mixture was warmed, and, on cooling, the anilinium salt of **7** crystallized out slowly as a white solid, 0.43 g (61%), mp 168–169 °C: ^{31}P NMR (DMSO/H_3PO_4 cap.) δ +17.3; ^1H NMR (DMSO/Me_4Si/one drop D_2O) δ 6.84–6.92 (m, 3 H, Ar), 7.16–7.58 (m, 6 H, Ar), 7.8 (app d, 7.5 Hz, 1 H, Ar), 8.2 (app d, 8 Hz, 1 H, H-8); ^{13}C NMR (DMSO/Me_4Si) δ 108.4 (d, 175.1 Hz, C_2), 115.8, 118.2, 118.35 (d, 13.0 Hz C_4), 123.1, 124.5 (d, 12.9 Hz, C_{8a}), 125.8, 127.3 (d, 6.7 Hz, C_3), 127.8, 128.4, 129.3, 136.1 (d, 2.3 Hz, C_{4a}), 146.1, 157.8 (d, 7.0 Hz, C_1).

Anal. Calcd for $C_{16}H_{16}NO_4P$; C, 60.57; H, 5.05; N, 4.42; P, 9.78. Found: C, 60.50; H, 5.10; N, 4.46; P, 9.94.

(3-Hydroxy-2-naphthyl)phosphonic Acid (8). Starting with 1.87 g of **6**, the yield of the crude acid **8** was 1.30 g (87%). For characterization, it was converted into the anilinium salt, yield 73%, white solid, mp 213–214 °C: ^{31}P NMR (DMSO/H_3PO_4 cap.) +13.4; ^1H NMR (DMSO/Me_4Si/one drop D_2O) 6.8–6.9 (m, 3 H, Ar), 7.1–7.2 (m, 3 H, Ar), 7.3 (t, 7 Hz, 1 H, Ar), 7.5 (t, 7 Hz, 1 H, Ar), 7.7 (d, 8 Hz, 1 H, Ar), 7.8, (d, 8 Hz, 1 H, Ar), 8.1 (d, 14.5 Hz, 1 H, Ar); ^{13}C NMR (DMSO/Me_4Si) δ 109.6 (d, 9.1 Hz), 116.4, 118.9, 121.6 (d, 173.2 Hz, C_2), 123.4, 126.2, 127.2 (d, 14.0 Hz, C_{8a}), 127.9, 128.7, 129.4, 133.8 (d, 4.6 Hz), 136.5, 145.1, 156.6 (d, 4.7 Hz, C_3).

Anal. Calcd for $C_{16}H_{16}NO_4P$: C, 60.57; H, 5.05; N, 4.42; P, 9.78. Found: C, 60.25; H, 5.12; N, 4.32; P, 9.83.

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Synthesis of Substituted Cyclic 1,3-Dienes via Selective 1,4-Elimination of Benzenesulfinic Acid from Allylic Phenyl Sulfones

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Conjugated dienes are useful substrates in organic synthesis. The classical use has been cycloaddition, but recently metal-mediated additions to these substrates have attracted considerable interest.[2] In our projects on palladium-catalyzed oxidation of conjugated dienes, there was a demand for specifically substituted conjugated dienes.[3] In our first approach to prepare these substrates, we studied alkylation of allylic aryl sulfoxides and subsequent thermal elimination.[4,5] However, this approach resulted

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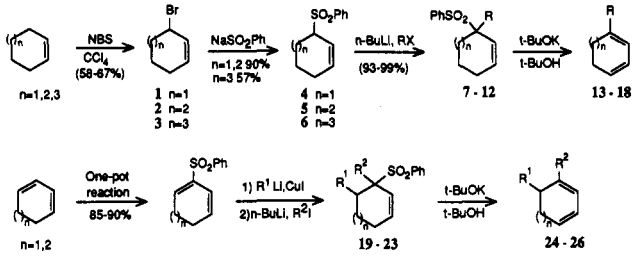
0022-3263/91/1956-0835$02.50/0

Scheme I



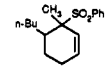
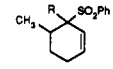
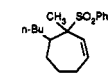
in a mixture of conjugated dienes. In connection with the sulfoxides, we also studied the corresponding sulfones and observed a remarkably high 1,4-selectivity in the elimination of benzenesulfinic acid from allylic sulfones. Selective 1,4-elimination of benzenesulfinic acid from allylic sulfones has previously been observed in acyclic systems.[6] We therefore decided to explore this reaction, and in this paper we report a general synthesis of substituted cyclic conjugated dienes via allylic sulfones.

Two main approaches for the preparation of substituted allylic sulfones were used (Scheme I). The first one starts with a cycloalkene, which on allylic bromination and subsequent reaction with sodium benzenesulfinate in *N,N*-dimethylformamide (DMF)[7] afforded an allylic sulfone in good yield. The allylic sulfone was regioselectively alkylated by formation of its lithium anion (*n*-BuLi, −78 °C) and subsequent reaction with the appropriate alkyl halide. Elimination of benzenesulfinic acid was performed by treatment of the allylic sulfone with potassium *tert*-butoxide in *tert*-butyl alcohol. This resulted in a highly 1,4-selective elimination to produce the 1-substituted 1,3-dienes (Table I). Other reaction conditions tried for the base-induced elimination such as sodium methoxide in methanol, lithium diisopropylamide (LDA) in tetrahydrofuran (THF), or 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in methylene chloride gave a lower yield and a less selective reaction.

The second approach utilizes a 1,3-cycloalkadiene as the starting material and leads to a specifically disubstituted conjugated diene. The starting diene was transformed to a 2-(phenylsulfonyl) 1,3-diene in one pot, either by sulfonylmercuration–elimination[8] or selenosulfonation–elimination.[9] Copper-catalyzed Michael addition of an alkyllithium to the sulfonyl diene[8b,10] and α-alkylation of the resulting sulfone afforded the desired disubstituted allylic sulfone. Again the selective 1,4-elimination of benzenesulfinic acid to give the 1,6-disubstituted 1,3-diene was performed by using potassium *tert*-butoxide in *tert*-butyl alcohol (Table I).

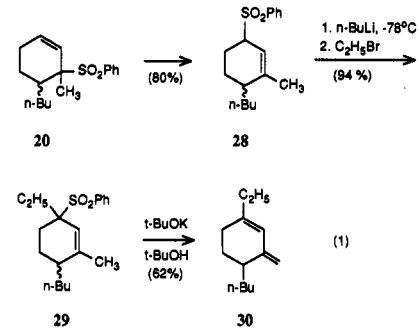
It is known that allylic sulfones can undergo a 1,3-rearrangement.[11] It occurred to us that such an allylic

Table I. 1,4-Elimination of Benzensulfinic Acid from Allylic Sulfones[a]

allyl sulfone			diene		
structure	R	no.	structure	no.	% yield[b]
	*n*-Bu	7		13	78
	CH_3	10		16	73
	*n*-Bu	8		14	83
	CH_3	11		17	68
	*n*-Bu	9		15	77
	CH_3	12		18	68
		20		24	60
	*n*-Bu	21		25	60
	CH_3	22		26	68
		23		27	85

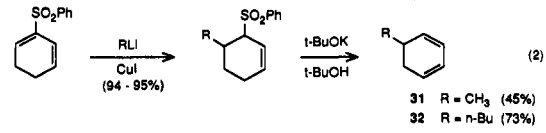
[a] All reactions were performed in *t*-BuOH at 80 °C, using *t*-BuOK as base (see Experimental Section). [b] Isolated yield.

rearrangement followed by α-alkylation would give a new allylic sulfone as a precursor for a diene. Thus, acid-catalyzed rearrangement of **20** afforded **28**, which on subsequent alkylation gave **29** (eq 1). Now, there are two



possibilities for 1,4-elimination of benzenesulfinic acid from **29**, one would give a 1,3-cyclohexadiene, the other a methylenecyclohexene. It turned out that the exocyclic elimination was highly favored from **29**, using the same reaction conditions as above, and **30** was the only product formed (>96% exocyclic diene).[12] This selectivity reflects the higher kinetic acidity of the allylic CH_3 compared to the other allylic proton.

All the substrates discussed so far have been tertiary allylic sulfones, but as shown in eq 2 the 1,4-elimination



can also be applied to secondary allylic sulfones. Thus, 5-substituted 1,3-cyclohexadienes are available via a Mi-

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(12) A similar selectivity for abstraction of a methyl proton has been observed in *t*-BuOK-promoted elimination of allylic ethers: Otera, J.; Niibo, Y.; Okuda, K. *Chem. Lett.* **1986**, 1829.

chael addition to 2-(phenylsulfonyl)-1,3-cyclohexadiene and subsequent elimination of benzenesulfinic acid. In this way **31** and **32** were obtained from 2-(phenylsulfonyl)-1,3-cyclohexadiene in overall yields of 42 and 69%, respectively.

The high selectivity for 1,4-elimination in these systems is remarkable.[13] The highly selective and smooth elimination should make the present diene synthesis a useful complement to previous methods. Many of the literature procedures[14] for the preparation of 1-substituted 1,3-cycloalkadienes give products that are contaminated with isomeric dienes, resulting in separation problems.

Experimental Section

General Remarks. ^1H and ^{13}C NMR spectra were recorded for $CDCl_3$ solutions at 300 and 75 MHz, respectively. IR spectra were obtained on neat samples (unless otherwise specified), and only the strongest/structurally most important peaks are reported. When necessary, reaction solvents were dried and distilled under nitrogen by using standard procedures, while reaction flasks and syringes were oven-dried (120 °C) before use. Merck silica gel (230–400 mesh) was used for flash chromatography. GC analyses were performed with a capillary gas chromatograph with a flame ionization detector. A 30-m DB-5 J&M fused silica column was used. All products were obtained as clear colorless oils unless otherwise stated.

3-Bromocyclohexene (1) was prepared in 60% yield via allylic bromination of cyclohexene with *N*-bromosuccinimide:[15] IR 3031, 2945, 1640, 1435, 1184, 861, 732 cm^{-1}; ^1H NMR δ 5.92–5.73 (m, 2 H, olefinic), 4.81 (m, 1 H, H-3), 2.32–1.60 (m, 6 H, allylic and homoallylic); ^{13}C NMR δ 130.75, 128.74, 48.67, 32.58, 24.50, 18.41.

3-Bromocycloheptene (2).[16] The same procedure as for **1** with cycloheptene afforded 16.34 g (58%) of **2**, which was used immediately in the next step: IR 3025, 2928, 1642, 1444, 763 cm^{-1}; ^1H NMR δ 5.92 (dd, J = 11.5, 6.0 Hz, 1 H, H-2), 5.83 (dt, J = 11.4, 5.7 Hz, 1 H, H-1), 4.93 (t (distorted), J = 6 Hz, 1 H, H-3), 2.27–1.40 M, 8 H, allylic, homoallylic, and H-5); ^{13}C NMR δ 135.27, 132.22, 53.56, 36.24, 28.22, 26.58, 26.36.

3-Bromocyclooctene (3). The same procedure with cyclooctene afforded 22.5 g (67%) of **3**. The bromide was used immediately in the next step: IR 3021, 2927, 1647, 1445, 776 cm^{-1}; ^1H NMR δ 5.82–5.73 (m, 1 H, H-2), 5.64–5.53 (m, 1 H, H-1), 4.98–4.88 (m, 1 H, H-3), 2.29–1.92 (m, 4 H, allylic, and H-4), 1.75–1.23 (m, 6 H, H-5, -6, and -7); ^{13}C NMR δ 133.21, 129.69, 48.86, 40.80, 28.94, 26.49, 26.07, 25.60.

3-(Phenylsulfonyl)cyclohexene (4).[17] According to the procedure of Schank,[7] sodium benzensulfinate (18.37 g, 112 mmol) was added to a solution of bromide **1** (10.63 g, 66.3 mmol) in DMF (200 mL) at 0 °C. The reaction mixture was stirred for 24 h and then poured into water (500 mL). The aqueous phase was extracted with ether/hexane (1:1, 3 × 50 mL) and the combined organic phases were washed with water (5 × 50 mL). After drying the organic phases ($MgSO_4$), the solvent was removed under reduced pressure. This yielded the desired product as a colorless viscous oil, which solidified upon standing, 13.2 g (90%): IR 2946, 1447, 1305, 1149, 1096 cm^{-1}; ^1H NMR δ 7.86–7.80 and 7.64–7.47 (m, 5 H, Ar), 6.08–5.99 (m, 1 H, H-1), 5.74 (dd, J = 10.2, 2.3 Hz, 1 H, H-2) 3.76–3.67 (m, 1 H, H-3), 1.99–1.65 and 1.52–1.37 (m, 6 H, allylic and homoallylic); ^{13}C NMR δ 137.25, 135.12, 133.46, 128.94, 128.81, 118.32, 61.62, 24.18, 22.51, 19.31.

Sulfones **5** and **6** were prepared from bromides **2** and **3** as described for **4**.

3-(Phenylsulfonyl)cycloheptene (5): yield, 14.15 g (90%) of white crystals; mp 97 °C; IR ($CDCl_3$) 2934, 1447, 1305, 1147, 1085 cm^{-1}; ^1H NMR δ 7.93–7.80 and 7.65–7.45 (m, 5 H, Ar), 6.30–5.92 (m, 1 H, H-1), 5.77 (dd, J = 11.5, 4.2 Hz, 1 H, H-2), 3.87–3.77 (m, 1 H, H-3), 2.33–2.08 (m, 2 H, allylic), 2.08–1.93 (m, 2 H, H-4), 1.74–1.32 (m, 4 H, H-6 and H-7); ^{13}C NMR δ 137.65, 136.71, 133.46, 128.88, 128.86, 125.59, 66.11, 27.79, 27.66, 26.71, 25.82. Anal. Calcd for $C_{13}H_{16}O_2S$: C, 66.07; H, 6.82. Found: C, 66.18; H, 6.75.

3-(Phenylsulfonyl)cyclooctene (6): yield, 8.75 g (53%) as white crystals; mp 127 °C; IR ($CDCl_3$) 2932, 2857, 1448, 1306, 1294, 1148, 1086, cm^{-1}; ^1H NMR δ 7.93–7.85 and 7.66–7.49 (m, 5 H, Ar), 5.85 (dq, J = 9.3, 1.1 Hz, 1 H, H-1), 5.60 (dt, J = 9.8, 1.2 Hz, 1 H, H-2), 4.08–3.98 (m, 1 H, H-3), 2.23–2.92 (m, 4 H, allylic and H-4), 1.74–1.32 (m, 4 H, H-5 and H-6); ^{13}C NMR δ 138.34, 134.93, 133.45, 128.93, 128.60, 122,49, 63.19, 28.70, 28.39, 26.56, 26.22, 24.62. Anal. Calcd for $C_{14}H_{18}O_2S$: C, 67.17; H, 7.25. Found: C, 67.27; H, 7.26.

3-*n*-Butyl-3-(phenylsulfonyl)cyclohexene (7). *n*-BuLi (2.0 mL, 4.4 mmol) was added to a THF (20 mL) solution of sulfone **4** (890 mg, 4 mmol) at −20 °C. After stirring the red solution for 15 min, 1-bromobutane (658 mg, 4.8 mmol) was added, and the cooling bath was removed. The reaction mixture was stirred for an additional hour and then poured into water (10 mL). The water layer was extracted with ether/hexane (1:1, 3 × 10 mL). The combined organic phases were washed with brine (10 mL) and dried ($MgSO_4$). The solvents were removed under reduced pressure. The crude product was eluted (hexane, hexane/ether, gradient) through a short silica-gel column, which gave 1.05 g (96%) of the desired product: IR 3029, 2957, 1446, 1299, 1144, 1083, 1071 cm^{-1}; ^1H NMR δ 7.87–7.78 and 7.63–7.44 (m, 5 H, Ar), 6.10 (dt, J = 10.2, 4.0 Hz, 1 H, H-1), 5.59 (d, J = 10.2 Hz, 1 H, H-2), 2.12–2.01 (m, 1 H, one of H-4), 1.93–1.66 (m, 5 H, one of H-4, H-6 and homoallylic in chain), 1.34–1.18 (m, 4 H, CH_2CH_2), 0.85 (t, J = 6.6 Hz, 3 H, Me); ^{13}C NMR δ 136.49, 135.8, 133.25, 133.40, 128.34, 123.81, 66.65, 34.54, 27.00, 26.24, 23.83, 23.11, 18.75, 13.79. Anal. Calcd for $C_{16}H_{22}O_2S$: C, 69.03; H, 7.96. Found: C, 68.81; H, 7.99.

Sulfones **8** and **9** were prepared by the same procedure as described for **7**.

3-*n*-Butyl-3-(phenylsulfonyl)cycloheptene (8): yield, 1.12 g (96%) of sulfone **8** after purification on a short silica-gel column; IR 2931, 1446, 1298, 1139, 1081 cm^{-1}; ^1H NMR δ 7.92–7.87 and 7.57–7.50 (m, 5 H, Ar), 6.04 (dq, J = 7.0, 4.8 Hz, 1 H, H-1), 5.43 (dd, J = 12.2, 2.0 Hz, 1 H, H-2), 2.25–2.04 (m, 2 H, allylic), 1.98–1.85 (m, 1 H, one of H-4), 1.80–1.58 (m, 5 H, one of H-4, H-5 and H-6), 1.52–1.18 (m, 6 H, $(CH_2)_3$), 0.88 (t, J = 7.2 Hz, 3 H, Me); ^{13}C NMR δ 137.76, 137.20, 133.24, 130.52, 128.41, 127.50, 72.98, 36.46, 31.04, 27.93, 26.98, 26.36, 23.97, 23.34, 13.88; MS (CI, isobutane) 293. Anal. Calcd for $C_{17}H_{24}O_2S$: C, 69.82; H, 8.27. Found: C, 69.66, H, 8.18.

3-*n*-Butyl-3-(phenylsulfonyl)cyclooctene (9): yield, 1.21 g (99%); IR 2933, 1447, 1378, 1284, 1140, 1081, cm^{-1}; ^1H NMR δ 7.88–7.83 and 7.64–7.46 (m, 5 H, Ar), 5.76 (dt, J = 11.9, 9.1 Hz, 1 H, H-1), 5.42 (δ, J = 11.9 Hz, 1 H, H-1), 2.34–2.14 (m, 2 H, allylic), 2.03–1.89 (m, 1 H, one of H-4), 1.87–1.18 (m, 13 H, one of H-4, all six of H-5, -6 and -7, and $(CH_2)_3$), 0.93 (t, J = 7.2 Hz, 3 H, Me); ^{13}C NMR δ 143.82, 135.17, 133.20, 130.95, 128.16, 127.76, 72.35, 35.86, 30.12, 26.27, 25.89, 25.61, 25.34, 23.98, 23.55, 13.90; MS (CI, isobutane) 307. Anal. Calcd for $C_{18}H_{26}O_2S$: C, 70.55; H, 8.55. Found: C, 70.43, H, 8.43.

3-Methyl-3-(phenylsulfonyl)cyclohexene (10). To a solution of sulfone **4** in THF (50 mL) at −70 °C was added *n*-BuLi (88.69 mL, 1.5 M, 13.0 mmol). The resulting red mixture was stirred for 15 min at −70 °C, and then methyl iodide (2.0 g, 14.2 mmol) was added. The cooling bath was removed and the yellow solution was stirred for an additional hour. The reaction mixture was poured into water (20 mL) and then the layers were separated. The aqueous phase was extracted with ether/hexane (1:1, 3 × 10 mL), and the combined organic phases were washed with brine (10 mL). The solvents were dried ($MgSO_4$) and then removed under reduced pressure. The crude product obtained was eluted through a short silica-gel column, which gave the desired sulfone **10**, 2.32 g (93%) as a clear colorless oil, which solidified upon

(13) (a) The lack of 1,2-elimination cannot be explained by an unfavored conformation since the phenylsulfonyl group of 3-cyclohexenyl sulfones has been shown to prefer an axial orientation.[13b] A likely explanation for the observed selectivity is therefore that kinetic anion formation completely controls the selectivity. (b) Trost, B. M.; Schmuff, N. R. *J. Am. Chem. Soc.* **1985**, *107*, 396.

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standing. Recrystallization from ethanol afforded white crystals, mp = 52 °C: IR 3030, 2938, 1738, 1446, 1300, 1144, 1073 cm^{-1}; ^1H NMR δ 7.95–7.86 and 7.72–7.50 (m, 5 H, Ar), 6.01 (dt, J = 10.1 Hz, 1 H, H-1), 5.72 (d (distorted), J = 10.2 Hz, 1 H, H-2), 2.16–1.46 (m, 6 H, allylic and homoallylic), 1.44 (s, 3 H, Me); ^{13}C NMR δ 135.80, 133.62, 133.31, 130.26, 128.36, 124.67, 63.48, 29.40, 24.16, 22.08, 18.31; MS (CI, isobutane) 237. Anal. Calcd for $C_{13}H_{16}O_2S$: C, 66.07; H, 6.82. Found: C, 65.89; H, 6.71.

Sulfones **11** and **12** were prepared according to the procedure described above for **10**.

3-Methyl-3-(phenylsulfonyl)cycloheptene (11): yield, 2.24 g (98%); IR 2934, 1446, 1299, 1144, 1070 cm^{-1}; ^1H NMR δ 7.97–7.82 and 7.67–7.46 (m, 5 H, Ar), 5.92 (m, 1 H, H-1), 5.56 (d, J = 11.8 Hz, 1 H, H-2), 2.18–1.74 (m, 5 H, two allylic, two H-4 and one of H-6), 1.69–1.47 (m, 3 H, one of H-6 and both of H-5), 1.44 (s, 3 H, Me); ^{13}C NMR δ 136.19, 135.94, 133.33, 130.48, 128.42, 128.33, 69.46, 32.07, 26.48, 22.89, 21.94 (two carbons superimposed); MS (CI, isobutane) 251.

3-Methyl-3-(phenylsulfonyl)cyclooctene (12): yield, 2.40 g (99%); IR 2931, 1446, 1302, 1145, 1070 cm^{-1}; ^1H NMR δ 7.90–7.78 and 7.68–7.43 (m, 5 H, Ar), 5.69 (dt, J = 9.1 Hz, 1 H, H-1), 5.42 (d, J = 11.8 Hz, 1 H, H-2), 2.39–2.27 (m, 1 H, one of H-4), 2.06–1.77 (m, 3 H, allylic and one of H-4), 1.73–1.25 (m, 6 H, H-5, -6, and H-7), 1.49 (s, 3 H, Me); ^{13}C NMR δ 135.344, 134.06, 133, 13.90, 128.56, 128.20, 69.33, 30.78, 25.27, 24.92, 23.90, 23.62, 20.69; MS (CI, isobutane) 265. Anal. Calcd for $C_{15}H_{20}O_2S$: C, 68.15; H, 7.62. Found: C, 68.05; H, 7.70.

1-*n*-Butyl-1,3-cyclohexadiene (13).[18] The sulfone **7** (9.58 g, 34.4 mmol) was dissolved together with potassium *tert*-butoxide (8.56 g, 76.4 mmol) in *tert*-butyl alcohol (96 mL) under an atmosphere of nitrogen. The mixture was stirred at 80 °C for 6 h. The mixture was allowed to cool to 20 °C and then poured into water (100 mL). The aqueous phase was extracted with pentane (2 × 20 mL), and the combined organic phases were washed with water (7 × 70 mL) and dried ($MgSO_4$). The solvent was distilled off until about 20 mL of the solvent–product mixture was left in the flask. The crude product solution was filtered through a short silica-gel column eluted with pentane, and then the solvent was removed by distillation. The product was Kugelrohr distilled, which afforded 3.64 g (78%) of diene **13**: IR 3038, 2928, 1466, 688 cm^{-1}; ^1H NMR δ 5.91–5.84 (m, 1 H, olefinic), 5.72–5.62 (m, 2 H, olefinic), 2.23–2.03 (m, 6 H, allylic), 1.37–1.20 (m, 6 H, $(CH_2)_3$), 0.89 (t, J = 7 Hz, 3 H, Me); ^{13}C NMR δ 140.18, 124.80, 123.35, 118.40, 37.10, 29.81, 26.53, 23.00, 22.45, 13.96.

Dienes **14–18** were prepared according to the procedure described for **13**.

1-*n*-Butyl-1,3-cycloheptadiene (14):[19] yield, 360 mg (83%): IR 3014, 2927, 1466, 909, 734 cm^{-1}; ^1H NMR δ 5.72–5.67 and 5.56–5.51 (m, 3 H, olefinic), 2.35–2.23 (m, 4 H, allylic in ring), 2.05 (t, J = 7 Hz, 2 H, allylic in chain), 1.83 (quint, 2 H, homoallylic in ring), 1.46–1.22 (m, 4 H, two methylene in chain), 0.90 (t, J = 7.2 Hz, 3 H, Me); ^{13}C NMR δ 146.65, 131.54, 125.00, 120.32, 40.46, 34.60, 32.07, 30.54, 25.89, 22.45, 13.96; HRMS calcd for $C_{11}H_{18}$ 150.1408, found 150.1409.

1-*n*-Butyl-1,3-cyclooctadiene (15):[20] yield, 420 mg (77%): IR 3004, 2927, 1449, 908, 735 cm^{-1}; ^1H NMR δ 5.75 (dd, J = 11.3, 3.9 Hz, 1 H, H-3), 5.63 (d, J = 4 Hz, 1 H, H-2), 5.56 (dt, J = 11.3, 6.4 Hz, 1 H, H-4), 2.20–1.98 (m, 6 H, allylic), 1.58–1.18 (m, 8 H, two methylenes in ring and in chain), 0.92 (t, J = 7.2 Hz, 3 H, Me); ^{13}C NMR δ 142.44, 130.37, 126.28, 121.35, 38.02, 30.86, 30.32, 29.04, 23.84, 23.31, 22.61, 13.98; MS (EI) 164.

1-Methyl-1,3-cyclohexadiene (16): yield, 4.37 g (73%); product was identified by comparison with a reference sample;[3a] ^1H NMR δ 5.88–5.80 (m, 1 H, olefinic); 5.66–5.58 (m, 2 H, olefinic), 2.23–2.02 (m, 4 H, allylic), 1.77 (s, 3 H, Me).

1-Methyl-1,3-cycloheptadiene (17):[21] yield, 700 mg (68%); IR 2926, 1446, 1302, 1144 cm^{-1}; ^1H NMR δ 5.71–5.66 (m, 2 H, olefinic), 5.60–5.54 (m, 1 H, olefinic), 2.36–2.27 (m, 4 H, allylic), 1.88–1.77 (m, 2 H, H-6), 1.82 (s, 3 H, Me); ^{13}C NMR δ 142.42, 131.43, 124.83, 120.83, 36.59, 31.65, 26.82, 25.32; MS (EI) 164.

1-Methyl-1,3-cyclooctadiene (18):[22] yield, 1.00 g (82%); IR 2926, 1446, 1302, 1145 cm^{-1}; ^1H NMR δ 5.80–5.71 (m, J = 11.4 Hz, 1 H, H-3), 5.69–5.63 (m, 1 H, H-2), 5.58 (dt, J = 11.4, 6.5 Hz, 1 H, H-4), 2.20–2.08 (m, 4 H, allylic), 1.78 (t, J = 1.3 Hz, 3 H, Me), 1.58–1.42 (m, 4 H, homoallylic); ^{13}C NMR δ 138.64, 130.53, 126.33, 121.76, 32.45, 28.87, 24.38, 23.39, 23.10; MS (EI) 122.

4-*n*-Butyl-3-(phenylsulfonyl)cycloheptene (19). To a chilled (−78 °C) THF solution of 3-(phenylsulfonyl)-1,3-cycloheptadiene[9] (612 mg, 2.6 mmol) and CuI (599 mg, 3.1 mmol) was added *n*-BuLi (2.6 mL, 6.78 mmol) during 10 min. The resulting mixture was stirred at −78 °C for 30 min, and then the cooling bath was removed. After additional stirring for 15 min, the reaction was quenched with saturated NH_4Cl (10 mL). The aqueous phase was extracted with diethyl ether (3 × 10 mL), and the combined organic phases were washed with brine and then dried ($MgSO_4$). The solvent was removed at reduced pressure and the crude product was eluted with (hexane/EtOAc, 9:1) through a short silica-gel column. Evaporation of the solvent gave the desired sulfone **19**, 750 mg (90%), as a 1:1 mixture of diastereomers, which was not separated: IR 2929, 1446, 1305, 1147, 1085 cm^{-1}. *trans*-**19**: ^1H NMR δ 7.95–7.84 and 7.69–7.50 (m, 5 H, Ar), 6.08–5.97 (m, 1 H, H1), 5.85–5.76 (m, 1 H, H2), 4.00 (m, 1 H, H3), 2.52–2.41 (m, 1 H, H4), 2.29–2.13 (m, 2 H, one of H7 and H5), 2.06–1.92 (m, 1 H, one of H7), 1.78–1.64 (m, 1 H, one of H8), 1.63–1.42 (m, one of H8, H5 and both of H6), 1.40–1.12 (m, 4 H, CH_2CH_2), 0.90 (t (distorted), 3 H, Me); ^{13}C NMR δ 139.42, 135.40, 133.42, 129.09, 128.47, 123.39, 69.12, 34.20, 33.77, 29.59, 28.23, 27.05, 22.73, 19.91, 14.11. *cis*-**19**: ^1H NMR δ 7.93–7.84 and 7.78–7.48 (m, 5 H, Ar), 6.13 (ddd, J = 11, 8, 3.5 Hz, 1 H, H1), 5.22 (ddd, J = 11, 8, 2.5 Hz, 1 H, H2), 3.65 (dd, J = 8, 3.5 Hz, 1 H, H3), 2.57–2.36 (m, 2 H, H4 and one of H7), 2.32–2.11 (m, 2 H, one of H5 and H7), 1.81–1.69 (m, 1 H, one of H5), 1.58–1.48 (m, 2 H, H6), 1.48–1.10 (m, 6 H, $(CH_2)_3$), 0.85 (t, J = 8 Hz, 3 H, Me); ^{13}C NMR δ 140.70, 139.54, 133.30, 128.86, 119.59, 70.60, 33.85, 32.38, 29.34, 29.24, 28.90, 22.58, 20.17, 14.00 (two carbons superimposed). Anal. Calcd for $C_{17}H_{24}O_2S$: C, 69.82; H, 8.27. Found: C, 69.55; H, 8.27.

3-Methyl-4-*n*-butyl-3-(phenylsulfonyl)cyclohexene (20). To a chilled (−78 °C) THF (40 mL) solution of 4-*n*-butyl-3-(phenylsulfonyl)cyclohexene[8b] (2.18 g, 7.9 mmol) was added *n*-BuLi (5.8 mL, 8.6 mmol). The resulting red solution was stirred for 1 h at −78 °C. MeI (1.42 g, 9.5 mmol) was added and the cooling bath was removed. The orange colored mixture was allowed to warm to 20 °C and then it was poured into water (20 mL). The layers were separated and the squeous phase was extracted with ether/pentane (1:1, 3 × 10 mL). The combined organic phases were washed with brine (10 mL) and then dried ($MgSO_4$). The solvent was removed under reduced pressure and the crude product was eluted with diethyl ether through a short silica-gel column. Removal of the solvent under reduced pressure afforded 1.58 g (68%) of sulfone **20**: IR 2958, 14447, 1293, 1146, 1064 cm^{-1}; ^1H NMR δ 7.78–7.81 and 7.64–7.46 (m, 5 H, Ar), 6.13–6.02 (m, 1 H, H-1), 5.76 (dd, J = 10.2, 2.1 Hz, 1 H, H-2), 5.01 (d, J = 10 Hz, 1 H, H-2), 2.36–1.84 (m, 4 H, allylic, H-4, and one of H-5), 1.67–0.97 (m, 10 H, $(CH_2)_3$, one of H-5, and Me), 0.96–0.83 (t (distorted), 3 H, Me in chain); ^{13}C NMR δ 139.16, 136.35, 133.76, 133.29, 133.23, 133.15, 130.45, 130.39, 128.38, 128.36, 127.27, 127.07, 68.49, 65.77, 45.31, 37.26, 31.14, 30.05, 29.68, 26.09, 25.35, 24.57, 23.99, 23.50, 23.28, 22.89, 22.53, 16.38, 14.17, 14.11; MS (CI, isobutane) 293. Anal. Calcd for $C_{17}H_{24}O_2S$: C, 69.82; H, 8.27. Found: C, 69.67; H, 8.11.

4-Methyl-3-*n*-butyl-3-(phenylsulfonyl)cyclohexene (21). To a chilled (−78 °C) THF (80 mL) solution of 4-methyl-3-(phenylsulfonyl)cyclohexene[8b] (3.7 g, 15.7 mmol) was added *n*-BuLi (11.5 mL, 17.2 mmol). The resulting red solution was stirred for 1 h at −78 °C. *n*-BuBr (2.58 g, 18.8 mmol) was added, and the cooling bath was removed. The reaction mixture was stirred overnight and then poured into water (20 mL). The two phases were separated and the aqueous layer was extracted with ether/hexane (1:1, 3 × 15 mL). The organic phases were washed with

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brine and dried ($MgSO_4$). Removal of the solvent under reduced pressure afforded the crude product, which was eluted with diethyl ether through a short silica-gel column, which gave after evaporation of the solvent 4.16 g (91%) of sulfone **21**: IR 3027, 2958, 1446, 1290, 1143, 1083 cm^{-1}; ^1H NMR δ 7.88–7.81 and 7.64–7.46 (m, 5 H, Ar), 6.13–6.02 (m, 1 H, H-1), 5.76 (dd, J = 10.2, 2.1 Hz, 1 H, H-2), 5.01 (d, J = 10 Hz, 1 H, H-2), 2.36–1.84 (m, 4 H, allylic H-4, and one of H-5), 1.67–0.97 (m, 10 H, $(CH_2)_3$, one H-5, and Me on ring), 0.96–0.83 (t (distorted), 3 H, Me on chain); ^{13}C NMR 139.09, 136.40, 135.32, 134.68, 133.13, 133.07, 130.57, 130.35, 128.30, 128.22, 125.24, 125.47, 72.63, 71.32, 41.54, 33.32, 32.41, 32.36, 29.32, 28.97, 27.80, 26.90, 26.06, 25.79, 25.70, 15.12, 24.71, 23.57, 23.24, 23.08; MS (CI, isobutane) 293. Anal. Calcd for $C_{17}H_{24}O_2S$: C, 69.82; H, 8.27. Found: C, 69.73; H, 8.17.

3,4-Dimethyl-3-(phenylsulfonyl)cyclohexene (22). The same reaction conditions as for the preparation of **21** were applied, but MeI was used as the alkylating reagent instead of *n*-BuBr. This afforded the desired sulfone **22** as a mixture of diastereomers (88:12) in 95% yield: IR 3029, 2932, 1446, 1298, 1145, 1071 cm^{-1}; ^1H NMR (major diastereomer) δ 7.95–7.85 and 7.72–7.50 (m, 5 H, Ar), 5.97–5.89 (m, 1 H, H-1), 5.67 (dq, J = 10.1, 1.4 Hz, 1 H, H-2), 2.15–1.56 (m, 4 H, H-6, H-4, and one H-5), 1.42 (s, 3 H, allylic Me), 1.42–1.23 (m, 1 H, one of H-5), 1.15 (d, J = 6.6 Hz, 3 H, homoallylic Me); ^{13}C NMR δ 136.20, 133.32, 133.12, 130.42, 128.42, 126.73, 68.09, 31.62, 27.95, 24.34, 17.11, 16.16; MS (CI, isobutane) 251. Anal. Calcd for $C_{14}H_{18}O_2S$: C, 67.17; H, 7.25. Found: C, 66.95, H, 7.10.

3-Methyl-4-*n*-butyl-3-(phenylsulfonyl)cycloheptene (23). Sulfone **19** was alkylated by using the same reaction conditions as for the preparation of **20**. This gave the desired sulfone **23** as a 4:1 mixture of diastereoisomers in 94% yield: IR 3029, 2928, 1446, 1300, 1144, 1072 cm^{-1}; ^1H NMR (major diastereomer) δ 7.90–7.83 and 7.65–7.47 (m, 5 H, Ar), 5.98 (dt, J = 12, 6 Hz, 1 H, H-1), 5.45 (d, J = 12 Hz, 1 H, H-2), 2.40–2.26 (m, 1 H, one of H-7), 2.24–1.96 (m, 3 H, one of H-7 and H-4), 1.94–1.48 (m, 4 H, H-6 and H-5), 1.39 (s, 3 H, allylic Me), 1.42–1.08 (m, 6 H, $(CH_2)_3$), 0.91 (t, J = 7 Hz, 3 H, Me in chain); ^{13}C NMR δ 138.54, 136.22, 133.20, 130.36, 129.80, 128.49, 72.23, 44.88, 31.22, 30.15, 29.68, 28.07, 24.90, 24.50, 22.78, 14.21. Anal. Calcd for $C_{18}H_{26}O_2S$: C, 70.55; H, 8.55. Found: C, 70.31; H, 8.52.

Dienes **24–27** were prepared from sulfones **21–23**, respectively, utilizing the same reaction conditions as described for **13**.

4-Methyl-5-*n*-butyl-1,3-cyclohexadiene (24):[23] yield, 410 mg (60%); IR 3040, 2928, 1445 cm^{-1}; ^1H NMR δ 5.85–5.78 (m, 1 H, H-2), 5.64 (d, J = 5.2 Hz, 1 H, H-3), 5.58–5.51 (m, 1 H, H-1), 2.42–2.28 (m, J_{gem} = 17.5, 8.6 Hz, 1 H, H-6_{ax}), 2.14 (ddd, J_{gem} = 17.5, 5, 5 Hz, 1 H, H-6_{eq}), 1.94 (m, 1 H, H-5), 1.80 (s, 3 H, Me on ring), 1.48–1.16 (m, 6 H, $(CH_2)_3$), 0.91 (t (distorted), 3 H, Me in chain); ^{13}C NMR δ 140.03, 124.29, 121.70, 118.82, 37.28, 29.67, 29.58, 27.21, 22.94, 22.01, 14.05.

5-Methyl-4-*n*-butyl-1,3-cyclohexadiene (25): yield, 1.14 g (60%); IR 3040, 2927, 1456 cm^{-1}; ^1H NMR δ 5.88–5.81 (m, 1 H, H-2), 5.62–5.52 (m, 2 H, H-1 and -3), 2.44–2.32 (m, J = 17, 9 Hz, 1 H, H-6_{ax}), 2.20–1.93 (m, 4 H, allylic), 1.53–1.23 (m, 7 H, Me on ring and $(CH_2)_2$), 0.94 (t (distorted), 3 H, Me on chain); ^{13}C NMR δ 145.09, 124.10, 121.66, 117.36, 34.81, 31.01, 30.49, 30.47, 22.55, 16.97, 13.97; HRMS calcd for $C_{11}H_{18}$ 150.1408, found 150.1409.

4,5-Dimethyl-1,3-cyclohexadiene (26): yield, 370 mg (62%); spectral data are in accord with those reported in the literature for **26**;[24] IR 2928, 1446 cm^{-1}; ^1H NMR δ 5.484–5.77 (m, 1 H, olefinic), 5.64–5.53 (m, 2 H, olefinic), 2.44–2.31 (m, J = 17.6, 8 Hz, 1 H, H-6_{ax}), 2.12 (sextet, J = 7 Hz, 1 H, H-5), 1.96 (dt, J = 17, 5.5 Hz, H-6_{eq}), 1.77 (s, 3 H, vinylic Me), 0.97 (d, J = 7 Hz, 3 H, allylic Me); ^{13}C NMR δ 140.60, 124.08, 121.82, 118.50, 32.02, 30.96, 21.47, 16.96.

4-Methyl-5-*n*-butyl-1,3-cycloheptadiene (27): yield, 155 mg (83%); IR 3012, 2925, 1448 cm^{-1}; ^1H NMR 5.67–5.64 (m, 2 H, H1 and H2), 5.53–5.48 (m, 1 H, H3), 2.37–2.21 (m, 3 H, allylic), 1.85 (s, 3 H, vinylic Me), 1.73–1.61 (m, 1 H, one of H6), 1.50–1.42 (m, 1 H, one of H6), 1.40–1.18 (m, 6 H, $(CH_2)_3$), 0.89 (t (distorted), 3 H, Me in chain); ^{13}C NMR δ 147.17, 131.59, 124.07, 119.54, 44.17, 30.14, 28.96, 27.13, 26.55, 22.91, 22.34, 14.09; MS (EI) 164.

3-Methylene-4-*n*-butyl-1-ethylcyclohexene (30). Sulfone **20** was rearranged under acidic conditions ($HOAc/H_2O$ (3/2), 100 °C, 1 h) to 2-methyl-3-*n*-butyl-6-(phenylsulfonyl)cyclohexene (**28**) in 80% yield.[11a] Deprotonation with *n*-BuLi at −78 °C and alkylation with ethyl bromide gave 2-methyl-3-*n*-butyl-6-ethyl-6-(phenylsulfonyl)cyclohexene (**29**) in 94% yield. The sulfone was then eliminated under the same reaction conditions as described for **13**. This afforded **30** in 62% yield: ^1H NMR δ 5.86 (s, 1 H, H2), 4.69 (d, J = 11.5 Hz, 2 H, exocyclic olefin), 2.36–1.88 (m, 5 H, allylic), 1.82–1.52 (m, 2 H, H5), 1.46–1.18 (m, 6 H, $(CH_2)_3$), 1.03 (t, J = 7.4 Hz, 3 H, Me in ethyl chain), 0.90 (br t, 3 H, Me in butyl chain); ^{13}C NMR δ 147.84, 143.00, 122.63, 108.29, 38.89, 32.34, 30.30, 29.47, 27.54, 25.87, 22.89, 14.14, 12.06.

5-Methyl-1,3-cyclohexadiene (31). 4-Methyl-3-(phenylsulfonyl)cyclohexene[8b] was eliminated under the same reaction conditions as described for **13**. This gave the desired diene and the 1-substituted isomer **16**, in a 95:5 ratio and 45% yield. Diene **31** was identified by comparison with an authentic sample:[3a] IR 3031, 2958, 1456, 680 cm^{-1}; ^1H NMR δ 5.92–5.60 (m, 4 H, olefinic), 2.50–2.16 (m, 2 H, one of H6 and H5), 2.02–1.02 (m, 1 H, one of H6), 1.04 (d, J = 6.9 Hz, 3 H, Me); ^{13}C NMR δ 133.20, 125.89, 123.89, 123.37, 30.58, 27.76, 19.79; MS (EI) 94.

5-*n*-Butyl-1,3-cyclohexadiene (32).[25] 4-*n*-Butyl-3-(phenylsulfonyl)cyclohexane[8b] was eliminated under the same reaction conditions as described for **13**. This gave the desired diene **32** and the 1-substituted isomer **13** in a 94:6 ratio and 73% yield: IR ($CDCl_2$) 3035, 2928, 1466 cm^{-1}; ^1H NMR δ 5.90–5.68 (m, 4 H, olefinic), 2.32–2.18 (m, 2 H, allylic, H5, and one of H6), 2.03–1.87 (m, 1 H, one H6), 1.48–1.20 (m, 6 H, $(CH_2)_3$), 0.92 (t (distorted), 3 H, Me); ^{13}C NMR δ 131.88, 126.01, 123.98, 123.44, 34.26, 32.87, 29.13, 28.70, 22.86, 14.10.

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Analysis of (α-Hydroxybenzyl)tetrahydroisoquinoline Stereoisomers by Pirkle Column HPLC: Correlation of Absolute Configuration with Order of Elution

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The analysis of absolute configuration by chiral stationary-phase HPLC is becoming ever more important to synthetic chemists as the number of compound classes separable by this method grows.[1] We have recently begun as investigation of enantiofacial selectivity in the addition of chiral organometallics to aldehydes,[2] a process that generates two new stereocenters in one step. The initial

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