Economical and Environmentally Friendly Syntheses of 2-(Phenylsulfonyl)-1,3-cyclohexadiene and 2-(Phenylsulfonyl)-1,3-cycloheptadiene[1]

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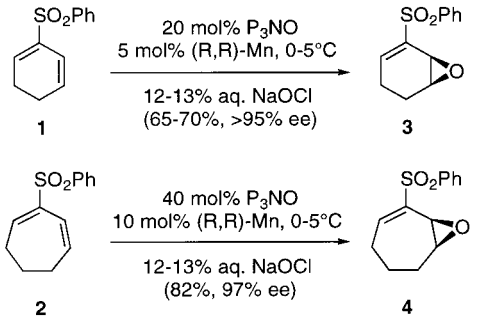
A large-scale and inexpensive synthesis of dienes **1** and **2** has been developed via a four-step procedure starting with benzenethiol and the corresponding cyclic ketone. No chromatography is required.

Introduction

An area of current research has focused on the chemistry of 6- and 7-ring vinyl sulfone epoxides,[2] **3** and **4**, obtained from Jacobsen catalytic asymmetric epoxidation[3] of 2-(phenylsulfonyl)-1,3-cyclohexadiene **1** and 2-(phenylsulfonyl)-1,3-cycloheptadiene **2**, respectively (Scheme 1). When this research was in its infancy, two simple and efficient methods by Bäckvall provided ample amounts of material for initial experiments. Bäckvall's synthesis of 2-(phenylsulfonyl)-1,3-cyclohexadiene **1** involves a phenylsulfonylmercuration of 1,3-cyclohexadiene[4] followed by the β-elimination of mercury(0) to form the 2-phenylsulfonyl-substituted diene.[5] The synthesis of 2-(phenylsulfonyl)-1,3-cycloheptadiene **2** is accomplished by a tandem selenosulfonation-oxidation[6] of 1,3-cycloheptadiene[7] with phenyl benzeneselenosulfonate. Now that both enantiomers of epoxides **3** and **4** are the mainstay of many research projects, the demand for 2-arylsulfonyl-1,3-cyclodienes[8] has increased manyfold in this research group and others.[9] Three main drawbacks to the above procedures exist: expense of the starting materials[10] and reagents,[11] toxicity of the reagents, and stoichiometric production of heavy metal waste. An alternative synthesis of dienes **1** and **2** is reported herein.

Scheme 1. Catalytic Jacobsen Asymmetric Epoxidation of Diene 1 and 2[a]



[a] P_3NO = 4-(3-phenylpropyl)pyridine *N*-oxide. ((*R*,*R*)-Mn) = (*R*,*R*)-(−)-*N*,*N*′-Bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediaminomagnesium(III) chloride.

Results and Discussion

The original synthetic plan involved conversion of the cyclic ketone to the enol thioether, followed by regioselective bromination. Oxidation of the corresponding phenyl sulfide to sulfone would then activate a base-catalyzed 1,4-elimination to yield the 2-substituted 1,3-diene. Numerous methods for the transformation of ketones to vinyl sulfides exist, but they involve multiple steps, corrosive Lewis acids, or moisture-sensitive anhydrides as reagents. Labiad found that enol thioethers could be efficiently synthesized from their respective cyclic ketones using acidic clay catalysis.[12] A slight modification of this procedure (longer reaction time and less catalyst) has produced phenyl vinyl sulfides **5** and **14** in 88% and 86% yield after distillation, respectively.

With the vinyl sulfides in hand, optimization of the regioselective bromination of **5** and **14** was undertaken. Trost and Lavoie have extensively studied the bromination of various vinyl sulfides[13] including **5**; however, their

(1) Synthesis via vinyl sulfones. 85. Chiral Carbon Collection. 9.

(2) (a) Hentemann, M. F.; Fuchs, P. L. *Tetrahedron Lett.* **1997**, *38*, 5615−5618. (b) Hentemann, M.; Fuchs, P. L. *Org. Lett.* **1999**, *1*, 355−357. (c) Jiang, W.; Lantrip, D. A.; Fuchs, P. L. *Org. Lett.* **2000**, *2*, 2181−2184.

(3) (a) Lee, N. H.; Jacobsen, E. N. *Tetrahedron Lett.* **1991**, *32*, 6533−6536. (b) Chang, S.; Heid, R. M.; Jacobsen, E. N. *Tetrahedron Lett.* **1994**, *35*, 669−672.

(4) 1,3-Cyclohexadiene was prepared in two steps from cyclohexene. Schaefer, J. P.; Endres, L. *Organic Syntheses*; Wiley: New York, 1973; Collect. Vol. V, pp 285−288.

(5) (a) Bäckvall, J. E.; Juntunen, S. K.; Andell, O. S. *Org. Synth.* **1989**, *68*, 148−154. (b) Andell, O. S.; Bäckvall, J. E. *Tetrahedron Lett.* **1985**, *26*, 4555−4558.

(6) (a) Bäckvall, J. E.; Najera, C.; Yus, M. *Tetrahedron Lett.* **1988**, *29*, 1445−1448. (b) Back, T. G.; Collins, S. *J. Org. Chem.* **1981**, *46*, 3249−3256.

(7) 1,3-Cycloheptadiene was prepared from the dissolving metal reduction of cycloheptatriene. Dirkzwager, H.; Nieuwstad, T. J.; Van Wijk, A. M.; Van Bekkum, H. *Recl. Trav. Chim. Pays-Bas* **1973**, *92*, 35−43.

(8) For a synthesis of 2-phenylsulfonyl-1,3-cyclooctadiene, see: Hardinger, S. A.; Fuchs, P. L. *J. Org. Chem.* **1987**, *52*, 2739−2749.

(9) For the most recent reviews of sulfone and sulfoxide chemistry and recent applications of 2-arylsulfonyl-1,3-dienes, see: Jonsson, S. Y.; Löfström, C. M. G.; Bäckvall, J. E. *J. Org. Chem.* **2000**, *65*, 8454−8457.

(10) Aldrich Chemical Co. (2000−2001): 1,3-cyclohexadiene, 100 mL, $244; 1,3-cycloheptadiene, 5 g, $146.

(11) For the synthesis of phenyl benzeneselenosulfonate, see: (a) Back, T. G.; Collins, S. *Tetrahedron Lett.* **1980**, *21*, 2213−2214. (b) Lin, H.-S.; Coghlan, M. J.; Paquette, L. A. *Org. Synth.* **1988**, *67*, 157−162.

(12) Labiad, B.; Villemin, D. *Synthesis* **1989**, 143−144.

(13) Trost, B. M.; Lavoie, A. C. *J. Am. Chem. Soc.* **1983**, *105*, 5075−5090.

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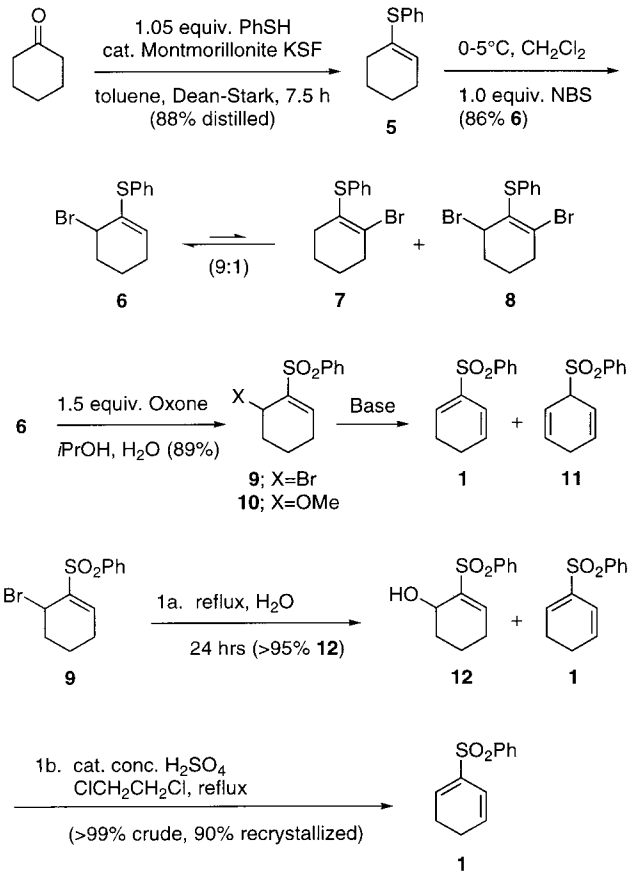
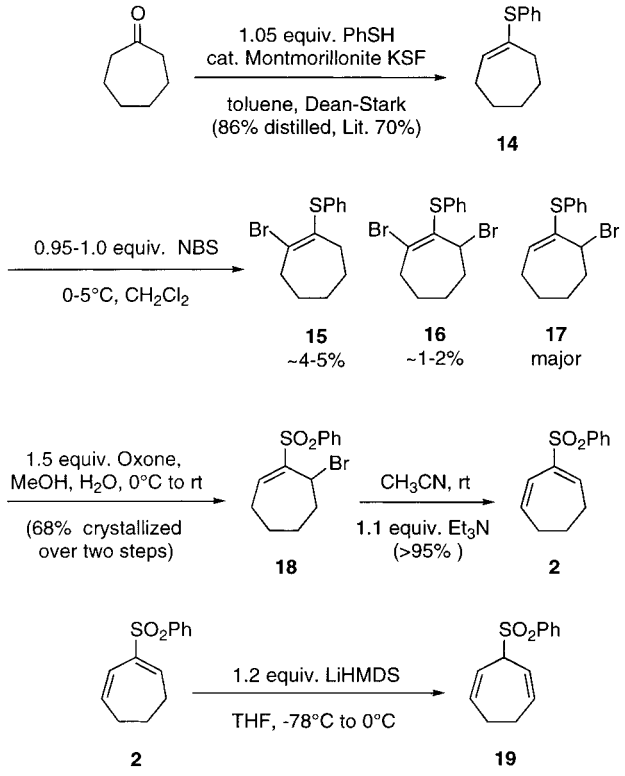
Scheme 2. Synthesis of 1



reported procedure led to an inseparable mixture of **6** and **7** in a ~3:2 ratio (Scheme 2). In our hands, bromination of **5** with a variety of bromine sources and conditions also resulted in the initial formation of approximately 1:1 mixtures of desired allylic bromide **6** and the vinyl bromide **7** along with trace amounts of the dibromide **8**. However, it was observed that a neat mixture of **6** and **7** equilibrates to an approximately 9:1 thermodynamic mixture with **6** as the major product. The equilibrated oil was diluted with hexanes and chilled in a freezer (−30 °C) to crystallize **6** selectively. The mother liquor was concentrated and reequilibrated, and the process was repeated three times to give **6** in 86% yield. Oxone oxidation of **6** in methanol and water resulted in conversion of the sulfide to the sulfone, but as the reaction progressed, byproduct allylic methyl ether **10** was formed in increasing amounts. Substitution of 2-propanol for methanol eliminated this problem. Bromide **9** was then submitted to basic conditions (tertiary amines, alkoxides) to facilitate elimination to produce diene **1**. These conditions readily generated diene **1**, but it was found that **1** subsequently reacted with base to form the very interesting isomerized 1,4-diene **11**. Attempts to minimize the formation of **11** or crystallize diene **1** selectively were unsuccessful.[14] To avoid formation of **11**, an acid-catalyzed elimination proved highly effective. Thus, bromide **9** was hydrolyzed to allylic alcohol **12** in water at reflux. After cooling, alcohol **12** crystallized from the reaction mixture, and the highly acidic water (pH = 1) was decanted. 1,2-Dichloroethane[15] and a catalytic amount of concentrated sulfuric acid were added to the resultant

(14) A table of selected conditions has been placed in the Supporting Information.

Scheme 3. Synthesis of 2

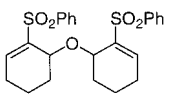


alcohol, which upon heating and water removal yielded **1** in near-quantitative yield. For most of our purposes, crude **1** could be directly used in the next reaction (Scheme 1), but recrystallized **1** could be obtained in 89% yield from diethyl ether.

Bromination of the analogous 7-ring vinyl sulfide **14** (Scheme 3) was unknown; thus, conditions for the formation of allylic bromide **17** were sought. After extensive optimization with numerous solvents, bases, and brominating agents, allylic bromide **17** was obtained as the major product along with 3−5% of vinyl bromide **15** and 1−2% of dibromide **16** as impurities. Oxidation[16] of the mixture led to the respective sulfones, which underwent selective crystallization of **18** in 68% over two steps. When exposed to triethylamine, bromide **18** smoothly underwent elimination to yield diene **2** in near-quantitative yield. Unlike the treatment of **9** with base, treatment of bromide **18** showed no evidence for the formation of 1,4-diene **19**, which was independently prepared in 10% yield. Diene **2** is obtained in 56% overall yield from cycloheptanone.

A brief explanation for the formation of the allylic, vinyl, and dibromides seen in Schemes 2 and 3 is presented in Scheme 4. For simplicity, only the 6-ring series is shown even though the mechanism is also applicable to the 7-ring series. Trost and Lavoie[13] provide a thorough explanation upon which much of this research

(15) If toluene is as the solvent, diene **1** is obtained in 80−85% yield with the remaining material as di(6-cyclohex-1-enesulfonyl)benzene ether **13**.



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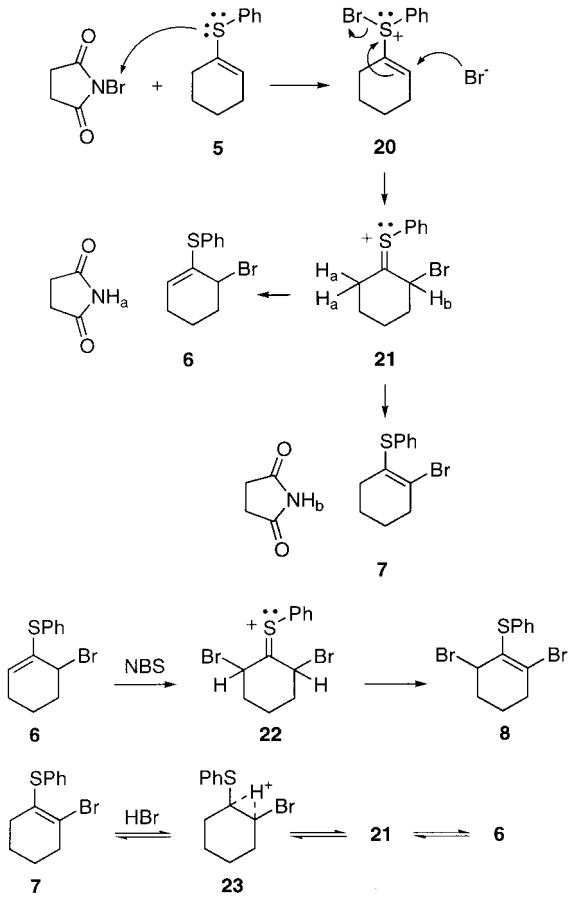
(16) Trost, B. M.; Curran, D. P. *Tetrahedron Lett.* **1981**, *22*, 1287−1290.

Scheme 4. Mechanism for the Formation of Allylic, Vinyl and Dibromides and the Equilibration between Bromides 6 and 7.



and mechanism is based. Formation of α-bromothionium ion **21** can be envisioned to result from initial sulfur-bromination of **20** followed by S_N2' trapping with the bromide anion. Alternatively, lone-pair-assisted electrophilic bromination could occur directly at the α-carbon center. Loss of either H_a or H_b would result in the formation of **6** or **7**, respectively. The increased acidity of H_b over H_a and the conformation of **21** contributes to the initial kinetic product distribution, but it is difficult to say which factor has the greatest effect. It is hypothesized that formation of dibromide **8** follows a similar path. The reaction of **6** with *N*-bromosuccinamide could also result in the direct formation of intermediate **22**. Unlike intermediate **21**, deprotonation of intermediate **22** would result in the exclusive formation of **8**.

It is hypothesized that the equilibration between **6** and **7** may be acid catalyzed. Hydrogen bromide could be formed by decomposition of the neat reaction mixture. Protonation of olefin **7** could again lead to intermediate **22**. Deprotonation by bromide would regenerate the acid catalyst and facilitate equilibration of the mixture between allylic bromide **6** and vinyl bromide **7**.

Conclusions

In conclusion, we have described an efficient route for the synthesis of 6- and 7-ring 2-substituted cyclic dienyl sulfones from inexpensive starting materials and reagents. We feel the avoidance of heavy metal wastes and the purification of all intermediates and products by distillation or cyrstallization make the new protocol attractive for large-scale synthesis.

Experimental Section

Silica gel (Silicycle, technical grade) used for filtration and flash chromatography was 230−400 mesh. Hexane was distilled before use, and acetonitrile and triethylamine were distilled from calcium hydride before use, but unless otherwise noted, all other solvents (toluene, dichloromethane, tetrahydrofuran, diethyl ether, 2-propanol, methanol) were used as received. Cyclohexanone (Aldrich), cycloheptanone (Aldrich), benzenethiol (97%, Aldrich), montmorillonite KSF (Aldrich), Oxone (Aldrich), and recently purchased *N*-bromosuccinamide (Acros) were all used as received. Melting points were obtained on a capillary melting point apparatus and are uncorrected.

2-(Phenylsulfonyl)-1,3-cyclohexadiene (1). 1,2-Dichloroethane (157 mL) and concentrated sulfuric acid (0.05 mL) were added to crude alcohol **12** (156.9 mmol) and heated at reflux. Concentrated sulfuric acid was added in 0.05 mL aliquots every 15 min until the alcohol was consumed as determined by TLC (ca. 4.5 h, 0.9 mL of concentrated H_2SO_4). Water formed during the reaction was removed with a modified Dean−Stark trap. After being cooled to ambient temperature, the solution was filtered through a pad of silica gel (ca. 7.5 g, 4 cm), and the flask and filter cake were washed with 1,2-dicholorethane. The resulting filtrate was concentrated under reduced pressure to yield a viscous oil. The oil was diluted with diethyl ether (10 mL) and placed in a −30 °C freezer. One crystallization of the oil provided 30.71 g (89%) of **1** as white crystals: mp 58−61 °C (lit.[5] 60−63 °C); R_f 0.53 (1:1 v/v ethyl acetate/hexane); ^{1}H and ^{13}C NMR agree with literature; ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.54, 22.06, 118.17, 127.46, 128.96, 129.87, 133.06, 134.64, 138.45, 139.67.

2-(Phenylsulfonyl)-1,3-cycloheptadiene (2). To a magnetically stirred solution of bromide **18** (90.82 g, 288 mmol) in 288 mL of acetonitrile was added triethylamine (44.2 mL, 317 mmol) in one portion. After 24 h at ambient temperature, the reaction was washed with 5% aqueous HCl and the aqueous layer extracted with ethyl acetate. The organic layers were combined, washed with brine, and dried ($MgSO_4$), and the volatiles were removed in vacuo to give **2** as a pale yellow solid (67.0 g, 99%): mp 57−58 °C (ether); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.85 (m, 2H), 2.31 (m, 2H), 2.56 (q, J = 5.8 Hz, 2H), 6.03 (m, 2H), 7.28 (t, J = 5.5 Hz, 1H), 7.46−7.64 (m, 3H), 7.84−7.90 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.53, 30.49, 30.97, 118.91, 127.61, 128.94, 132.90, 138.01, 139.15, 140.00, 141.85.

1-(Phenylthio)cyclohexene (5). To a solution of cyclohexanone (111 g, 1.13 mol) in toluene (260 mL) was added a slurry of montmorillonite KSF (10 g) in 20 mL of toluene. An additional 20 mL of toluene was used to wash any remaining montmorillonite KSF into the reaction flask. Thiophenol (118.6 g, 1.07 mol) was added, and the mixture was heated at reflux for 7.5 h with magnetic stirring. Water formed during the reaction was removed with a Dean−Stark trap. After being cooled to ambient temperature, the mixture was filtered to remove the montmorillonite KSF and the filter cake washed with hexanes. The solution was concentrated in vacuo and the remaining oil distilled (95−105 °C, 0.1 mmHg) through a 20 cm Vigreux column to yield 180.0 g (88%) of **5** as a pale yellow oil. This reaction was scaled up to 5.309 mol of thiophenol (603.05 g, Aldrich, 97% pure) and 5.57 mol of cyclohexanone (547.14 g) in 750 mL of toluene. The ratio of montmorillonite KSF was maintained at approximately 10 wt % to that of the ketone. Mechanical stirring is recommended for reactions greater than 1 mol. Ona large scale, distillation provided 891.3 g in 88% yield: R_f 0.38 (hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.57−1.72 (m, 4H), 2.11−2.20 (m, 4H), 6.07 (m, 1H), 7.16−7.33 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.50, 23.43, 26.56, 29.79, 126.01, 128.60, 129.87, 131.25, 132.41, 135.09.

6-Bromo-1-(phenylthio)cyclohexene (6). To an ice−water-cooled solution of 1-(phenylthio)cyclohexene **5** (200.2 g, 1.05 mole) in 700 mL of CH_2Cl_2 was added *N*-bromosuccinimide (NBS) in portions (ca. 5−10 g) in order to maintain the

reaction temperature below 10 °C. NBS (ca. 0.95−1.0 equiv) was added until the starting material was consumed as determined by TLC. Excess NBS lowered the yield and resulted in the formation of dibromide **8**. Care was taken to powder any lumps of NBS with a mortar and pestle before addition to the reaction mixture. Once complete, the reaction was washed with water, and the aqueous layer was extracted with hexanes. The organic layers were combined, and the volatiles were removed in vacuo. The neat oil was aged at ambient temperature until **6** and **7** had equilibrated to approximately a 9:1 ratio. The equilibration usually occurred during workup or within 1−2 h, but it has been known to require as much as 24 h of aging. The dark brown oil was diluted with 200 mL of hexanes and vacuum filtered through silica gel (10−15 g, 55 mm Büchner funnel, filter paper was also placed above the pad of silica gel). The pad of silica gel was washed with 200−300 mL of hexanes, and the total volume was reduced to 200−300 mL. The solution is placed in a −30 °C freezer until crystallization ceased (ca. 12 h). After the crystals were harvested, the volatiles were removed from the mother liquor, and the oil was reequilibrated. This process was repeated (a total of four recrystallizations) to provide **6** (244.9 g, 86%) as pale yellow/tan crystals: mp 30.5−31.5 °C; R_f 0.18 (hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.7−1.8 (m, 1H), 1.92−2.20 (m, 2H), 2.22−2.44 (m, 3H), 4.65 (m, 1H), 6.19 (t, J = 4.0 Hz, 1H), 7.2−7.44 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.65 (e), 26.69 (e), 33.21 (e), 50.91 (o), 127.10 (o), 129.08 (o), 130.94 (o), 134.03 (e), 134.13 (e), 136.93 (o). Anal. Calcd for $C_{12}H_{13}BrS$: C, 53.54; H, 4.87. Found: C, 53.69; H, 4.83. Compounds **7** and **8** were isolated by flash column chromatography and/or recrystallization from the mother liquor. Dibromide **8** constitutes approximately <5% of the crude reaction mixture as determined by ^{1}H NMR.

1-Bromo-2-(phenylthio)cyclohexene (7): clear colorless oil; R_f 0.29 (hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.68 (m, 4H), 2.05 (m, 2H), 2.63 (m, 2H), 4.65 (m, 1H), 7.20−7.44 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 23.09, 24.25, 31.86, 37.33, 122.72, 123.89, 127.48, 128.79, 131.54, 132.60.

1,3-Dibromo-2-(phenylthio)cyclohexene (8): pale yellow crystals; mp 38−39 °C; R_f 0.18 (hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.74−1.88 (m, 1H), 1.88−2.06 (m, 1H), 2.16−2.38 (m, 2H), 2.76−2.94 (m, 2H), 5.14 (m, 1H), 4.57 (s, 1H), 7.50−7.56 (m, 2H), 7.24−7.38 (m, 3H), 7.38−7.46 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.55, 32.66, 37.42, 50.98, 127.79, 129.15, 131.97, 132.10, 132.25, 133.70. Anal. Calcd for $C_{12}H_{12}Br_2S$: C, 41.40; H, 3.47. Found: C, 41.43; H, 3.09.

1-(Phenylsulfonyl)-6-bromocyclohexene (9). To a solution of bromide **6** (50.06 g, 186 mmol) in THF (100 mL) was added 2-propanol (750 mL). The solution was then cooled with an ice−water bath, and a solution of aqueous Oxone (171.5 g, 279 mmol, in 750 mL of deionized water) was added in portions under mechanical stirring. The reaction temperature was maintained below 30 °C during the addition of the Oxone solution. After approximately half of the oxone solution had been added, the ice−water bath was removed and the remaining Oxone solution added in one portion. The slurry was stirred for 14 h at ambient temperature. Upon completion, the slurry was filtered and the 2-propanol removed from the water in vacuo. The filter cake was washed with 2-propanol and added to the above filtrate. The aqueous layer was extracted with ethyl acetate and dried (anhydrous $MgSO_4$), and the volatiles were removed to afford **9** (49.85 g, 89%) as white crystals: mp 73−74 °C; R_f 0.53 (1:1 v/v ethyl acetate/hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.74−1.85 (m, 1H), 1.90−2.10 (m, 2H), 2.18−2.32 (m, 1H), 2.37−2.52 (m, 1H), 2.52−2.66 (m, 1H), 5.14 (m, 1H), 7.29 (dd, J = 3.1, 4.3 Hz, 1H), 7.50−7.56 (m, 2H), 7.59−7.64 (m, 1H), 7.91−7.96 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.87, 25.74, 32.46, 40.79, 128.45, 128.85, 133.41, 140.19, 141.69, 143.59. Anal. Calcd for $C_{12}H_{13}BrO_2S$: C, 47.85; H, 4.35. Found: C, 48.04; H, 4.34.

1-(Phenylsulfonyl)-6-methoxycyclohexene (10): colorless oil; R_f 0.46 (1:1 v/v ethyl acetate/hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.38−1.52 (m, 1H), 1.54−1.72 (m, 2H), 1.98−2.10 (m, 1H), 2.12−2.28 (m, 1H), 2.32−2.45 (m, 1H), 3.16 (s, 3H), 4.20 (m, 1H), 7.23 (dd, J = 2.9, 4.9 Hz, 1H), 7.47−7.60 (m, 3H), 7.87−7.90 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.43 (e), 25.66 (e), 25.78 (e), 56.32 (o), 70.47 (o), 127.55 (o), 128.44 (o), 132.61 (o), 140.62 (e), 141.35 (e), 143.20 (o). Anal. Calcd for $C_{13}H_{16}O_3S$: C, 61.88; H, 6.39. Found: C, 61.50; H, 6.36.

3-(Phenylsulfonyl)-1,4-cyclohexadiene (11): white crystals; mp 80−87 °C dec; R_f 0.53 (1:1 v/v ethyl acetate/hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.97−2.02, 2.05−2.10 (m, 1H), 2.46−2.52, 2.54−2.59 (m, 1H), 4.43 (m, 1H), 5.87−6.00 (m, 4H), 7.45−7.52 (m, 2H), 7.59−7.64 (m, 1H), 7.79−7.82 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 26.42, 63.59, 118.31, 128.25, 130.07, 132.34, 133.45, 135.45. Anal. Calcd for $C_{12}H_{12}O_2S$: C, 65.43; H, 5.49. Found: C, 65.06; H, 5.44.

2-(Phenylsulfonyl)cyclohex-2-enol (12). A mixture of bromide **9** (20.03 g, 66.49 mmol) and deionized water (100 mL) was heated at reflux (biphasic) for 12 h. Hydrogen bromide gas generated during the reaction was vented to an alkali trap. The reaction was allowed to cool to ambient temperature, and the mixture was aged 12 h. During that time, white crystals of alcohol **12** formed, and the water was decanted. Deionized water (100 mL) was added to the crude crystals of alcohol **12** and heated a reflux for an additional 12 h. The reaction was allowed to cool to ambient temperature, and the mixture was aged 12 h. The crystals were then washed several times with deionized water to remove all traces of hydrogen bromide. The crude product was used in the next reaction without purification: white crystals; mp 100−101 °C; R_f 0.32 (1:1 v/v ethyl acetate/hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.41−1.55 (m, 1H), 1.57−1.70 (m, 1H), 1.73−1.90 (m, 1H), 1.90−2.00 (m, 1H), 2.11−2.26 (m, 1H), 2.36−2.50 (m, 1H), 2.95 (bs, 1H), 4.33 (m, 1H), 7.20 (dd, J = 2.8, 4.9 Hz, 1H), 7.55 (m, 2H), 7.64 (m, 1H), 7.88−7.93 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.67 (e), 26.06 (e), 29.82 (e), 61.34 (o), 127.84 (o), 129.16 (o), 133.39 (o), 139.40 (e), 141.21 (e), 142.98 (o). Anal. Calcd for $C_{12}H_{14}O_3S$: C, 60.48; H, 5.92. Found: C, 60.58; H, 6.00.

Di(6-cyclohex-1-enesulfonyl)benzene ether (13): white crystals; R_f 0.30 (1:99 v/v MeOH/$CHCl_3$); mp 202−204 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.20−1.34 (m, 2H), 1.46−1.64 (m, 4H), 2.06−2.34 (m, 6H), 4.42 (m, 2H), 7.13 (dd, J = 3.1, 4.5 Hz, 2H), 7.41 (m, 6H), 7.53 (m, 4H), 7.74−7.77 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.21 (e), 25.84 (e), 26.17 (e), 65.48 (o), 127.19 (o), 128.65 (o), 132.60 (o), 139.66 (e), 141.35 (e), 146.06 (o). Anal. Calcd for $C_{24}H_{26}O_5S_2$: C, 62.86; H, 5.71. Found: C, 62.50; H, 5.71.

1-(Phenylthio)cycloheptene (14). Preparation of **14** followed the procedure described above for the synthesis of **5** using cycloheptanone (540 g, 4.81 mol), montmorillonite KSF (50 g), and thiophenol (557 g, 5.05 mol) in toluene (200 mL). The mixture was vigorously heated at reflux for 48 h with mechanical stirring. The crude oil was distilled (120−125 °C, 0.1 mmHg) through a 20 cm Vigreux column to obtain **14** (845.9 g, 86% yield) as a pale yellow oil: R_f 0.31 (hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.52−1.57 (m, 4H), 1.72−1.77 (m, 2H), 2.18−2.20 (m, 2H), 2.34−2.36 (m, 2H), 6.16 (t, J = 6.4 Hz, 1H), 7.18−7.22 (m, 1H), 7.27−7.33 (m, 4H), 7.88−7.94 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 26.70, 27.02, 29.28, 31.86, 35.21, 126.25, 128.72, 130.23, 135.48, 135.60, 137.18.

1,3-Dibromo-2-(phenylthio)cycloheptene (16). Under an inert atmosphere of argon was added dropwise bromine (5.3 mL, 102.7 mmol) to a stirred solution of **7** (10.0 g, 481.9 mmol) and pyridine (11.9 mL, 146.8 mmol, distilled from CaH_2) in dry CH_2Cl_2 (100 mL) at −78 °C. The reaction and cooling bath were allowed to slowly warm to room temperature over ∼10 h. The reaction was washed with 10% aqueous Na_2SO_3 and 5% aqueous HCl and dried (anhyd $MgSO_4$). The volatiles removed in vacuo to afford **16** (17.4 g, 98%) as a yellow solid. An analytical sample is prepared by recrystallization from hexanes: pale yellow crystals; mp 86−88 °C (hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.56−1.68 (m, 2H), 1.72−1.86 (m, 2H), 1.90−2.14 (m, 4H), 2.98 (dd, J = 6.4, 15.6 Hz, 1 H), 3.18 (ddd, J = 1.5, 11.6, 16.2 Hz, 1H), 4.81 (dd, J = 2.2, 6.1 Hz, 1H), 7.28−7.38 (m, 3H), 7.40−7.45 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.52, 25.70, 35.15, 41.74, 54.47, 127.89, 129.28, 131.73, 133.22, 135.13, 135.98. Anal. Calcd for $C_{13}H_{14}Br_2S$: C, 43.12; H, 3.90. Found: C, 43.13; H, 3.77.

7-Bromo-1-(phenylthio)cycloheptene (17). Preparation of **17** followed the procedure described above for the synthesis of **6** using **14** (87.25 g, 0.427 mol) in 425 mL of CH_2Cl_2. The dark brown oil was diluted with 100 mL of hexanes and vacuum filtered through silica gel (10−15 g, 55 mm Büchner funnel, filter paper was also placed above the pad of silica gel). The pad of silica gel was washed with 100−200 mL of hexanes, and the volatiles were removed in vacuo to give a pale yellow oil which was used in the next step without purification. A crystalline analytical sample was prepared by adding an equal volume of hexanes to the crude oil and chilling the solution in a −30 °C freezer overnight: mp <25 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.40−1.56 (m, 1H), 1.76−2.04 (m, 3H), 2.04−2.24 (m, 2H), 2.24−2.46 (m, 2H), 4.75 (d, J = 5,6 Hz, 1H), 6.42 (ddd, J = 1.1, 5.3, 7.7 Hz, 1H), 7.18−7.40 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.21, 26.41, 29.00, 35.64, 56.68, 126.73, 128.92, 129.98, 134.91, 136.68, 142.59.

1-(Phenylsulfonyl)-7-bromocycloheptene (18). The crude mixture of bromides **15**−**17** (combined ∼0.427 mol) was dissolved in 1.7 L of methanol and cooled using an ice−water bath. A solution of aqueous Oxone (393.7 g, 640.5 mmol, in 1.7 L deionized water) was added in portions under mechanical stirring. The reaction temperature was maintained below 30 °C during the addition of the Oxone solution. After approximately half of the oxone solution had been added, the ice−water bath was removed and the remaining oxone solution was added in one portion. The slurry was stirred for 14 h at 25 °C. Upon completion, the slurry was filtered and the methanol removed from the water in vacuo. The filter cake was washed with methanol and added to the above filtrate. The aqueous layer was extracted with ethyl acetate and dried (anhydrous $MgSO_4$), and the volatiles were removed to afford a viscous oil. The oil was dissolved in diethyl ether and placed in a −30 °C freezer. Three crops produced 91.4 g of **18** as a white solid in 68% yield: mp 68−70 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.30−1.48 (m, 1H), 1.67−1.81 (m, 1H), 1.84−2.04 (m, 2H), 2.04−2.26 (m, 2H), 2.36.2.50 (m, 1H), 2.50−2.64 (m, 1H), 5.15 (d, J = 5.3 Hz, 1H), 7.49 (ddd, J = 1.4, 4.5, 9.0, 1H), 7.51−7.59 (m, 2H), 7.60−7.67 (m, 1H), 7.87−7.93 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.17, 26.35, 28.05, 34.84, 46.18, 128.12, 128.98, 133.35, 139.13, 144.41, 147.96. Anal. Calcd for $C_{13}H_{15}BrO_2S$: C, 49.53; H, 4.80. Found: C, 49.79; H, 4.89. 1-Phenylsulfonyl-2-bromocycloheptene and 2-phenylsulfonyl-1,3-dibromocycloheptene were isolated by flash column chromatography and/or recrystallization from the mother liquor.

1-(Phenylsulfonyl)-2-bromocycloheptene: colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.48−1.66 (m, 4H), 1.72−1.84 (m, 2H), 2.85 (m, 2H), 2.92 (m, 2H), 7.48−7.58 (m, 2H), 7.58−7.64 (m, 1H), 7.90−7.96 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.70, 25.07, 30.17, 30.72, 44.66, 127.56, 128.70, 133.14, 136.26, 140.42, 143.31. Anal. Calcd for $C_{13}H_{15}BrO_2S$: C, 49.53; H, 4.80. Found: C, 49.81; H, 4.81.

2-(Phenylsulfonyl)-1,3-dibromocycloheptene: light tan needles; mp 118−122 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.52−1.70 (m, 1H), 1.82−2.06 (m, 3H), 2.08−2.36 (m, 2H), 2.91 (m, J = 1.5, 6.8, 15.6 Hz, 1H), 3.42 (ddd, J = 1.7, 11.9, 15.6 Hz, 1H), 6.18 (dd, J = 2.3, 6.0 Hz, 1H), 7.50−7.58 (m, 2H), 7.60−7.66 (m, 1H), 8.03−8.08 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.19, 25.75, 34.74, 44.32, 47.78, 128.17, 128.59, 133.41, 139.93, 144.02, 144.83. Anal. Calcd for $C_{13}H_{14}Br_2O_2S$: C, 39.62; H, 3.58. Found: C, 39.79; H, 3.53.

3-(Phenylsulfonyl)-1,4-cycloheptadiene (19). Under an inert atmosphere of argon was added dropwise LiHMDS (16.1 mL, 16.1 mmol, 1 M THF) to a stirred solution of **2** (3.14 g, 13.4 mmol) in dry THF (54 mL) at −78 °C. After being stirred at −78 °C for 10 min, the reaction was warmed to 0 °C for 15 min. The reaction was quenched with 5% aqueous HCl, the aqueous layer was extracted with ethyl acetate, the combined organic layers were dried (anhydrous $MgSO_4$), and the volatiles were removed to afford a viscous oil. Flash chromatography provided 2.286 g of a yellow semicrystalline solid. Recrystallization provided **19** (331 mg, 10% yield) as white crystals: mp 91−93 °C (Et_2O/Hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.52−1.57 (m, 4H), 4.49 (m, J = 6.1 Hz, 1H), 5.71 (m, J = 6.1, 11.4 Hz, 2H), 6.10 (m, J = 11.3 Hz, 2H), 7.50 (m, 2H), 7.62 (m, 1H), 7.82−7.86 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.15 (e), 68.87 (o), 120.48 (o), 128.39 (o), 129.78 (o), 133.55 (o), 136.43 (e), 138.27 (o). Anal. Calcd for $C_{13}H_{14}O_2S$: C, 66.64; H, 6.02. Found: C, 66.66; H, 5.92.

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Supporting Information Available: ^{13}C and ^{1}H spectra for compounds **1**, **2**, **5**−**14**, and **16**−**19** and the corresponding sulfones of **15** and **16**. A table of selected conditions for the transformation of **6** into dienes **1** and **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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