Table I. Ethylation Products of Nitrobenzene with Ethanol in Sulfuric Acid at 110 °C for 6 h

position of ethyl	t_R, min	content, %	position of ethyl	t_R, min	content, %
none	7.910	51.87	3,4-	20.433	1.24
2-	11.473	9.51	2,3,6-	20.712	0.15
3-	13.076	28.17	2,3,5-	23.025	0.19
4-	14.398	4.62	2,3,4-	23.869	0.08
2,6-	14.669	0.15	2,4,5-	24.326	0.09
2,3-	16.916	0.67	3,4,5-	26.880	0.07
2,5-	17.408	1.82	2,3,5,6-	26.555	0.03
2,4-	17.664	0.27	2,3,4,5-	30.004	0.02
3,5-	19.215	1.05	2,3,4,5,6-	32.114	0.01

believe that both the (limited) success of the reaction in the presence of an excess of the catalyst, as well as the unexpectedly high regioselectivity observed under these conditions, can be explained in light of a mechanism in which the reaction takes place on a coordinated rather than free substrate.

It is well known that $AlCl_3$ coordinates strongly with the meta-directing groups of the substrate. Thus, when only a small amount of $AlCl_3$ is added, its catalytic activity is lost as it coordinates preferentially with the substrate rather than the reagent, usually an alkyl halide. On the other hand, when at least a 2 molar excess of the catalyst is used, the first mole coordinates with the substrate, leaving the second to react with the reagent, thus generating the carbocation. The positive charge incurred in the coordinated substrate is concentrated at the ortho and para positions, which explains why only the meta isomer is obtained under these conditions. The fact that the reaction proceeds with only very limited reactivity is understood in light of the fact that the coordinated substrate is more positively charged than the free. Similar results were found for the alkylation performed in super acid.[8]

In view of the above findings, we ventured to formulate a plan for reactivating these substrates with respect to alkylation, based on the following considerations: (a) The inert nature of benzenes with meta-directing substituents toward Friedel–Crafts alkylation is a direct result of the preferential coordination of the $AlCl_3$ catalyst to the substrate rather than the alkyl halide reagent. (b) The alkyl cation must be an extraordinarily active electrophile, since it can react with the coordinated and, therefore, further deactivated substrate. (c) If an alternative catalyst is used, which will react preferentially with the reagent rather than the substrate, a change in mechanism may be observed, in which reaction takes place on the free, rather than coordinated, substrate. One would then expect to see greater reactivity, as well as lower selectivity for the reaction, much as is observed in other Friedel–Crafts alkylations.

We now report that the foregoing ideas have been confirmed, as evidenced by our successful ethylation of nitrobenzene in sulfuric acid,[9] using ethanol as the reagent. The latter is well known to be a much stronger base than the nitro group; hence, its success in competing with the substrate for the acid "catalyst". As shown in Table I, 17 of the 19 possible products were detected. The *o*-, *m*-, and *p*-nitroethylbenzenes were formed in a ratio of 19:70:11, respectively (mean of three runs). This distribution represents much lower selectivity than that observed in the nitration of nitrobenzene and is consistent with the poor selectivity found in Friedel–Crafts alkylations involving benzenes with ortho- and para-directing substituents.[4] These results constitute both the first example of Friedel–Crafts alkylation successfully applied to nitrobenzene, as well as the first example of Friedel–Crafts alkylation of an uncoordinated substrate bearing a meta-directing group.

The assignment of the isomers was based on mass spectral data, the GC retention times with linearly programmed temperature (assuming that the increment due to an ethyl group ortho, meta, or para to the nitro group remains constant), and comparison with the results obtained upon ethylation of *o*- and *p*-nitrobenzenes under similar conditions.[10]

Based on these promising early results, work has already been initiated involving the alkylations of various benzenes with meta-directing substituents using alcohols as the source of R^+, in a variety of protonic acids. Preliminary results are encouraging, and we hope to uncover a general synthetic strategy to the class of compounds bearing an alkyl group in the position meta to a meta-directing substituent, which thus far have not easily been prepared.

Experimental Section

Nitrobenzene (2.46 g, 20 mmol), ethanol (1.84 g, 40 mmol), and sulfuric acid (20 mL) were mixed and heated with stirring at 110 °C for 6 h. The mixture was then poured into water, extracted with chloroform, and subjected to analysis by GC-MS (HP-5988-A).

Acknowledgment. We wish to thank Julia A. Novak for editorial assistance.

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(9) Although sulfuric acid was used as the solvent in these reactions, no competing sulfonation of the substrates was observed. According to C. Courtot (*Compt. Rend.* **1926**, *182*, 855), the strength of the sulfonating agent is expressed by the π value. The π value needed for sulfonation of nitrobenzene (or nitrotoluenes) is 82, higher than that of 100% sulfuric acid. Thus, it appears that fuming sulfuric acid would be necessary in order to sulfonate these compounds. The acid used in our experiments was ca. 97% and was further diluted both by the ethanol present and the water formed in the reaction. On the other hand, the "yields" indicated were estimated based on the average number of ethyl groups on the ring and were found to be 86% and 92% in two runs. Thus, it appears that there are no extensive side reactions in the process.

(10) In spite of repeated efforts, we were not able to successfully accomplish the separation of the major components on a preparative scale, owing to their highly similar chromatographic behavior. These components have thus far only been separated by means of a capillary column.

A New Route to Functionalized Cyclohexane Derivatives via Epoxy Sulfone Cyclizations[1]

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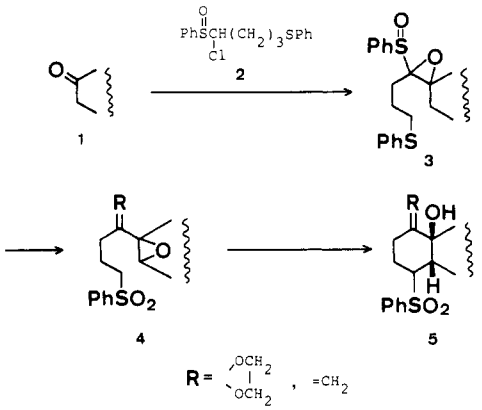
In the synthesis of six-membered carbocycles, which are widely found in natural products, numerous methods have been developed for efficient and stereospecific carbocyclic annulation.[2] Recently, we reported a novel method for annulation of ketones through α,β-epoxy sulfoxides by the

(1) α,β-Epoxy sulfoxides as useful intermediates in organic synthesis. 24. Part 23: Satoh, T.; Sugimoto, A.; Itoh, M.; Yamakawa, K. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 2942.

(2) See, for example: Ho, T.-L. *Carbocycle Construction in Terpene Synthesis*; VCH Publishers, Inc.: Weinheim, **1988**. Annulation by using epoxides: Rao, A. S.; Paknikar, S. K.; Kirtane, J. G. *Tetrahedron* **1983**, *39*, 2323. Smith, J. G. *Synthesis* **1984**, 629. Cooke, M. P., Jr.; Houpis, I. N. *Tetrahedron Lett.* **1985**, *26*, 3643. Molander, G. A.; Shubert, D. C. *J. Am. Chem. Soc.* **1987**, *109*, 576. Procter, G.; Russell, A. T.; Murphy, P. J.; Tan, T. S.; Mather, A. N. *Tetrahedron* **1988**, *44*, 3953.

0022-3263/90/1955-3962$02.50/0

Scheme I



use of a radical cyclization.[3] In continuation of our studies, we report here a new route to highly functionalized cyclohexane derivatives **5** from ketones **1** and 1-chloro-4-(phenylthio)butyl phenyl sulfoxide **2** through α,β-epoxy sulfoxides **3** and epoxy sulfones **4** (Scheme I).

A representative example of this method using cyclohexanone as the ketone is reported (Scheme II). α,β-Epoxy sulfoxide **6** was synthesized from 1-chloro-4-(phenylthio)butyl phenyl sulfoxide **2**, easily prepared from 4-chloro-1-butanol[4] and cyclohexanone in two steps in 95% overall yield. Heating **6** with 2 equiv of $LiClO_4 \cdot 3H_2O$ and 1 equiv of n-Bu_3PO in refluxing toluene gave cleanly the enone sulfide **7** in 94% yield.[5] Protection of the carbonyl group of **7** was carried out with a large excess ethylene glycol under standard conditions to afford the desired ketal **8** in quantitative yield as a colorless oil. In this step, no double-bond migration was observed. The reaction of **8** with 3.5 equiv of 3-chloroperoxybenzoic acid (MCPBA) (CH_2Cl_2, saturated $NaHCO_3$, room temperature for 4 h) afforded the desired epoxy sulfone **9** in quantitative yield as colorless crystals.

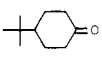
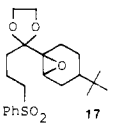
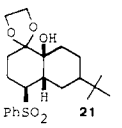
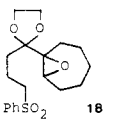
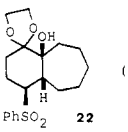
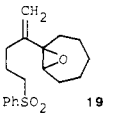
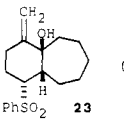
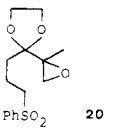
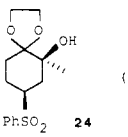
A study of epoxy sulfone cyclization[6] of **9** was made with strong bases such as n-BuLi, lithium diisopropylamide (LDA), or $LiN[Si(CH_3)_3]_2$ in tetrahydrofuran (THF) at −60 °C to room temperature, and it was found that excess (3–4 equiv) LDA in THF at −60 to 0 °C is the preferred reagent. Under these reaction conditions, **9** gave the cyclized product **10** as the sole product in 78% yield.

The structure of **10** was determined as follows. Based on Stork's epoxy nitrile cyclization,[7] the epoxy sulfone cyclization was thought to give decalin-type compound **10**; however, 5-*exo*-*trig* cyclization[8] (giving the five-membered spirocyclic product) is another possibility. In order to know the size of the produced ring, the ethylene ketal of **10** was deprotected with p-TsOH to give **11**. The ketone group of **11** showed a peak at 1725 cm^{-1} in its IR spectrum, which indicated the ring size to be six.[9] The stereochemistry of the phenylsulfonyl group and the conformation of **10** were determined from inspection of its NMR spectrum. The proton at the carbon bearing the phenylsulfonyl group showed a peak at δ 3.41 (1 H, m) with the width at half-height of 25 Hz in its NMR spectrum. This considerable value indicates the phenylsulfonyl group to be equatorial and the *cis*-decalin system to have a steroidal conformation.

Desulfonylation of **10**, which may be important in application of this procedure in practical synthesis, was achieved under standard conditions[10] (Na-Hg)[11] to afford **12** in good yield.

In order to extend this procedure to the synthesis of decalin derivatives having an *exo*-methylene group, **7** was converted to the epoxy sulfone **14** via α,β-epoxy ketone **13** under standard reactions in 68% overall yield. Epoxy sulfone cyclization of **14** was carried out under similar conditions as above to give a mixture of cyclized products (**15** and **16**; a ratio of 1:5) in 91% yield. Isomerization of **15** and/or **16** under basic conditions (t-BuOK/t-BuOH) gave a **15**:**16** = 1:3 mixture, which indicates that these products are isomers with respect to the sulfonyl group. Ozonolysis of the minor product **15** gave ketone **11** in quantitative yield. It is interesting to note that ketal **9** cyclizes with high stereoselectivity whereas the *exo*-methylene **14** gives two products. In the cyclization of **14**, **15** was initially formed and then the amount of **16** increased with the passage of time (observed on TLC). From this fact it is assumed that **15** is a kinetically controlled product and **16** is a thermodynamically stable compound. In the case of the cyclization of **9**, *cis*-decalin **10** is a kinetically controlled product and also must be a thermodynamically stable compound.

Table I. Preparation of Highly Functionalized Cyclohexane Derivatives from Ketones through Epoxy Sulfones

ketone	epoxy sulfone (%)[a]	product (%)[b]
	 (71)	 (84)[d]
	 (84)[c]	 (86)
..	 (67)	 (85)[e]
CH_3COCH_3	 (80)[c]	 (76)

[a] The overall yield from the α,β-epoxy sulfoxide. [b] The yield in the step of the epoxy sulfone cyclization. [c] These two epoxy sulfones were derived from the corresponding enone–sulfides by sequential treatment with 2.2 equiv of MCPBA (enone–sulfone), ethylene glycol (ketal), and then 1.1 equiv of MCPBA. [d] A diastereomeric mixture with respect to the *tert*-butyl group. [e] Sole product.

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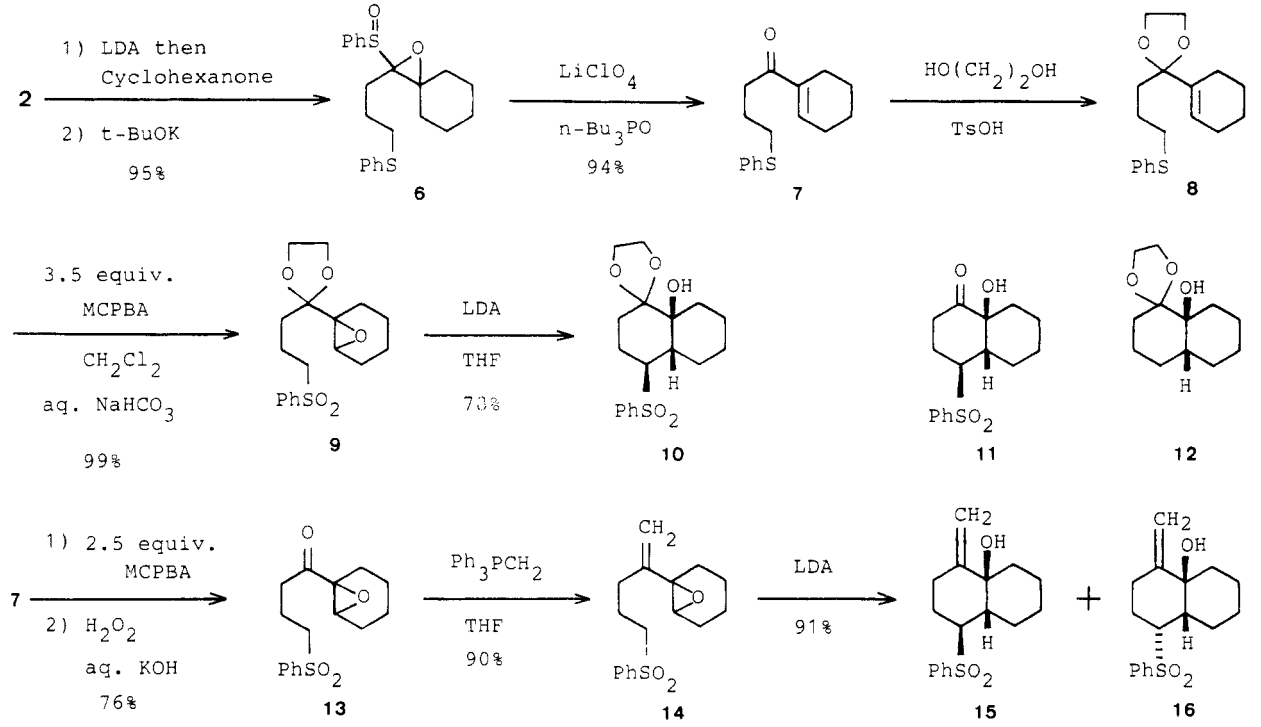
(11) Holleman, A. F. *Organic Syntheses*; Wiley: New York, 1967; Collect. Vol. I, p 554.

Scheme II



Representative examples of the synthesis of highly functionalized cyclohexane derivatives from ketones (except cyclohexanone) are shown in Table I. High yields were obtained at each step.

Extension of this procedure to the synthesis of compounds having larger ring sizes (7- and 14-membered rings) was studied; however, the epoxy sulfone cyclization step proved unsuccessful.

Experimental Section

All melting points are uncorrected. ^{1}H NMR spectra were measured in $CDCl_3$ at 100 MHz. Electron-impact mass spectra (MS) were obtained at 70 eV by direct insertion. Silica gel BW-127 ZH (Fuji-Davison) containing 2% fluorescence 254 and a quartz column were used for column chromatography, and the products having UV absorption were detected by UV irradiation. In experiments requiring dry solvents, THF was distilled from benzophenone ketyl; diisopropylamine and toluene were dried over CaH_2 and distilled. Some new compounds, especially oily products, did not give acceptable data for combustion analysis; however, the purity of all the title compounds was judged to be over 95% by ^{1}H NMR spectral determination and chromatographic analyses (GC and/or TLC).

2′-(Phenylsulfinyl)-2′-(3-(phenylthio)propyl)spiro[cyclohexane-1,1′-oxirane] (6). To a solution of LDA (1.15 mmol) in 3 mL of dry THF at −60 °C was added dropwise, with stirring, a solution of **2** (330 mg, 1 mmol) in 1 mL of THF. The mixture was stirred for 15 min, and then cyclohexanone (1.15 mmol) was added; after 5 min, the reaction was quenched with saturated aqueous NH_4Cl solution. The usual workup followed by silica gel column chromatography gave 415 mg (98%) of the adduct. *t*-BuOK (1.2 mmol) was added to a solution of the adduct in a mixture of *t*-BuOH–THF (5:1; 6 mL), and the mixture was stirred at room temperature for 10 min and then quenched with powdered NH_4Cl. The solvent was evaporated, and the residue was extracted with ether–benzene. The usual workup followed by silica gel column chromatography gave **6** (368 mg, 98%) as a colorless oil: IR (neat) 1090, 1050; ^{1}H NMR δ 1.2–1.9 (10 H, m), 1.9–2.3 (4 H, m), 2.58 (2 H, t, J = 7 Hz), 7.0–7.8 (10 H, m).

1-(1-Cyclohexenyl)-4-(phenylthio)-1-butanone (7). A solution of **6** (1.53 g, 3.95 mmol), $LiClO_4 \cdot 3H_2O$ (7.9 mmol), and Bu_3PO (4 mmol), in toluene (20 mL) was refluxed under N_2 for 4.5 h. The reaction mixture was diluted with benzene and was washed with water. The usual workup followed by silica gel column chromatography gave **7** (970 mg, 94%) as a colorless oil: IR (neat) 1670, 1640; ^{1}H NMR δ 1.58 (4 H, m), 1.93 (2 H, m), 2.19 (4 H, m), 2.77 (2 H, t, J = 7 Hz), 2.94 (2 H, t, J = 7 Hz), 6.83 (1 H, m), 7.0–7.4 (5 H, m); MS m/z (relative intensity) 260 (M^+, 11), 151 ([M − PhS]$^+$, 55), 136 (100); mass found m/z 260.1223, calcd for $C_{16}H_{20}OS$ (M) 260.1233.

1-(1-Cyclohexenyl)-4-(phenylthio)-1-butanone Ethylene Ketal (8). A solution of **7** (306 mg, 1.18 mmol), *p*-TsOH (0.38 mmol), and ethylene glycol (3.7 g) in 15 mL of benzene was refluxed for 8 h with azeotropic removal of water. The usual workup followed by silica gel column chromatography gave **8** (356 mg, 99%) as a colorless oil: IR (neat) 1490, 1440, 1045; ^{1}H NMR δ 1.3–2.3 (12 H, m), 2.7–3.0 (2 H, m), 3.82 (4 H, m), 5.79 (1 H, m), 7.0–7.4 (5 H, m); MS m/z (relative intensity) 304 (M^+, 8), 260 ([M − C_2H_4O]$^+$, 4), 223 (12), 153 (100); mass found m/z 304.1520, calcd for $C_{18}H_{24}O_2S$ (M) 304.1496.

1-(1,2-Epoxycyclohexyl)-4-(phenylsulfonyl)-1-butanone Ethylene Ketal (9). 3-Chloroperoxybenzoic acid (4.78 mmol) was added to a solution of **8** (363 mg, 1.19 mmol) in CH_2Cl_2 (10 mL) and saturated aqueous $NaHCO_3$ (5 mL), and the reaction mixture was stirred at room temperature for 4 h. The reaction mixture was diluted with ether, and the organic layer was washed with 10% NaOH. The usual workup followed by silica gel column chromatography afforded **9** (416 mg, 99%) as colorless crystals: mp 74–75 °C (AcOEt–hexane); IR (KBr) 1300, 1140; ^{1}H NMR δ 1.0–2.1 (12 H, m), 3.0–3.3 (3 H, m), 3.6–4.0 (4 H, m), 7.4–7.7 (3 H, m), 7.7–8.0 (2 H, m); MS m/z (relative intensity) 352 (M^+, trace), 255 (100). Anal. Calcd for $C_{18}H_{24}O_5S$: C, 61.34; H, 6.86; S, 9.10. Found: C, 61.50; H, 7.00; S, 9.01.

Epoxy Sulfone Cyclization of 9. A solution of **9** (102 mg, 0.29 mmol) in 0.5 mL of THF was added, with stirring, to a solution of LDA (0.87 mmol) in 2 mL of THF at −60 °C under N_2. The reaction mixture was stirred at −60 °C for 10 min, at 0 °C for 1 h, and finally at room temperature for 10 min. The reaction was quenched by adding saturated aqueous NH_4Cl, and the whole was extracted with ether. The usual workup followed by silica gel column chromatography gave **10** (82 mg, 78%) as colorless crystals: mp 171–173 °C (AcOEt–hexane); IR (KBr) 3530 (OH), 1310, 1150; ^{1}H NMR δ 1.4–1.8 (10 H, m), 1.9–2.1 (3 H, m), 2.36 (1 H, m), 3.41 (1 H, m), 3.8–4.1 (4 H, m), 7.4–7.9 (5 H, m). Anal. Calcd for $C_{18}H_{24}O_5S$: C, 61.34; H, 6.86; S, 9.10. Found: C, 61.37; H, 6.95; S, 9.08.

(4*R,4a*R**,8a*R**)-8a-Hydroxy-4-(phenylsulfonyl)decahydro-1-naphthalenone (11).** A solution of **10** (35 mg; 0.1 mmol) and *p*-TsOH·H_2O (0.02 mmol) in 2 mL of acetone was stirred at

50 °C for 3 h. To the reaction mixture was added saturated aqueous $NaHCO_3$, and the whole was extracted with ether–benzene. The usual workup followed by silica gel column chromatography gave 27 mg (91%) of **11** as colorless crystals: mp 206–207 °C (AcOEt–hexane); IR (KBr) 3470 (OH), 1725 (CO), 1310, 1150; ^{1}H NMR δ 1.1–2.9 (13 H, m), 3.5–3.9 (2 H, m), 7.4–8.0 (5 H, m). Anal. Calcd for $C_{16}H_{20}O_4S$: C, 62.32; H, 6.54; S, 10.40. Found: C, 62.15; H, 6.54; S, 10.44.

(4a*R,8a*S**)-8a-Hydroxydecahydro-1-naphthalenone Ethylene Ketal (12).** A suspension of **10** (97 mg, 0.27 mmol), 6% Na–Hg (1.08 mmol), and Na_2HPO_4 (1.08 mmol) in 3 mL of MeOH was stirred at room temperature for 26 h. Excess Na–Hg was filtered off, the filtrate was diluted with ether–benzene, and the solution was washed with saturated aqueous NH_4Cl. The usual workup followed by silica gel column chromatography gave 35 mg (61%; 89% conversion yield) of **12** as a colorless oil: IR (neat) 3525 (OH); ^{1}H NMR δ 1.1–1.4 (15 H, m), 3.72 (1 H, s), 3.98 (4 H, m); MS *m/z* (relative intensity) 212 (M^+, 14), 194 ($[M - H_2O]^+$, 20), 99 (100); mass found *m/z* 212.1408, calcd for $C_{12}H_{20}O_3$ (M) 212.1411.

1-(1,2-Epoxycyclohexyl)-4-(phenylsulfonyl)-1-butanone (13). To a solution of **7** (80 mg, 0.31 mmol) in 3 mL of CH_2Cl_2 was added MCPBA (0.77 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 10 min and then at room temperature for 1 h. The solution was diluted with CH_2Cl_2 and washed with 10% NaOH solution. Evaporation of the solvent gave the sulfone as a colorless oil. To a solution of the sulfone in 2 mL of ethanol was added 1.6 mL of 30% H_2O_2 and 6 N KOH (0.1 mmol), and the reaction mixture was stirred at room temperature for 6 h. The reaction mixture was diluted with water, and the whole was extracted with ether–benzene. The usual workup followed by silica gel column chromatography afforded **13** (70 mg, 76%) as a colorless oil: IR (neat) 1710 (CO), 1315, 1155; ^{1}H NMR δ 1.2–2.2 (9 H, m), 2.3–2.7 (3 H, m), 3.0–3.3 (3 H, m), 7.4–8.0 (5 H, m); MS *m/z* (relative intensity) 308 (M^+, 31), 211 (($[M - C_6H_9O]^+$, 82), 183 (57), 97 (100); mass found *m/z* 308.1082, calcd for $C_{16}H_{20}O_4S$ (M) 308.1081.

2-(1,2-Epoxycyclohexyl)-5-(phenylsulfonyl)-1-pentene (14). To a mixture of methyltriphenylphosphonium iodide (132 mg, 0.29 mmol) and *t*-BuOK (0.29 mmol) in a flame-dried flask was added dry THF (3 mL), and the suspension was stirred at room temperature for 15 min. To this yellow suspension was added a solution of **13** (65 mg, 0.21 mmol), and the mixture was stirred for 30 min. The reaction was quenched with saturated aqueous NH_4Cl; then the whole was extracted with ether. The usual workup followed by silica gel column chromatography gave **14** (58 mg, 90%) as a colorless oil: IR (neat) 1650, 1310, 1155; ^{1}H NMR δ 0.9–1.3 (12 H, m), 2.86 (1 H, m), 2.9–3.2 (2 H, m), 4.79 (1 H, m), 5.07 (1 H, m), 7.4–8.0 (5 H, m); MS *m/z* (relative intensity) 306 (M^+, 20), 278 (3), 211 (5), 164 ($[M - PhSO_2H]^+$, 20), 137 (100); mass found *m/z* 306.1300, calcd for $C_{17}H_{22}O_3S$ (M) 306.1289.

(4*R,4a*R**,8a*R**)-8a-Hydroxy-1-methylene-4-(phenylsulfonyl)decahydronaphthalene (15) and Its 4*R**,4a*S**,8a*S** Isomer (16).** **14** was cyclized in a similar way as described for **9** to give a mixture of **15** and **16** (**15**:**16** = 1:5) in 91% yield. **15**: colorless crystals; mp 165–166 °C (AcOEt–hexane); IR (KBr) 3580 (OH), 1655, 1305, 1120; ^{1}H NMR δ 1.2–2.4 (12 H, m), 2.4–2.7 (2 H, m), 3.16–4.48 (1 H, m), 4.80 (1 H, m), 5.02 (1 H, s), 7.4–8.0 (5 H, m). MS *m/z* (relative intensity) 306 (M^+, 3), 165 ($[M - PhSO_2]^+$, 29), 147 (100); mass found *m/z* 306.1299, calcd for $C_{17}H_{22}O_3S$ (M) 306.1289. Anal. Calcd for $C_{17}H_{22}O_3S$: C, 66.70; H, 7.24; S, 10.47. Found: C, 66.32; H, 7.31; S, 10.26. **16**: colorless crystals; mp 161–162 °C (AcOEt–hexane); IR (KBr) 3510 (OH), 1660, 1315, 1300, 1155; ^{1}H NMR δ 1.0–2.7 (14 H, m), 3.68–3.96 (1 H, m), 4.97 (1 H, s), 5.02 (1 H, m), 7.4–8.0 (5 H, m); MS *m/z* (relative intensity) 306 (M^+, 3), 165 ($[M - PhSO_2]^+$, 19), 147 (100); mass found *m/z* 306.1279, calcd for $C_{17}H_{22}O_3S$ (M) 306.1289. Anal. Calcd for $C_{17}H_{22}O_3S$: C, 66.70; H, 7.24; S, 10.47. Found: C, 66.66; H, 7.35; S, 10.42.

Ozonolysis of 15. A solution of **15** (55 mg; 0.18 mmol) in CH_2Cl_2 (1 mL) and MeOH (4 mL) was treated with excess O_3 at −60 °C. After all **15** reacted, dimethyl sulfide (2.5 mL) was added to the reaction mixture, and the solution was stirred at −60 °C for 10 min and then at room temperature for 1 h. The solvent was evaporated off, and the residue was purified by silica gel column chromatography to give 49 mg (89%) of **11**.

Epoxy sulfones 17–20 in Table I were synthesized from **2** and the corresponding ketones in a similar way as described above. **17**: colorless oil; IR (neat) 1310, 1150; ^{1}H NMR δ 0.81 (9 H, s), 0.9–2.1 (11 H, m), 3.0–3.3 (3 H, m), 3.7–4.0 (4 H, m), 7.4–8.0 (5 H, m). **18**: colorless oil; IR (neat) 1310, 1155; ^{1}H NMR δ 0.8–2.3 (14 H, m), 2.9–3.3 (3 H, m), 3.8–4.0 (4 H, m), 7.4–8.0 (5 H, m); MS *m/z* (relative intensity) 366 (M^+, trace), 322 ($[M - C_2H_4O]^+$, 0.5), 255 (100); mass found *m/z* 366.1501, calcd for $C_{19}H_{26}O_5S$ (M) 366.1499. **19**: colorless oil; IR (neat) 1650, 1310, 1155; ^{1}H NMR δ 1.0–2.3 (14 H, m), 2.82 (1 H, t, *J* = 5 Hz), 3.08 (2 H, m), 4.76 (1 H, m), 5.03 (1 H, m), 7.4–8.0 (5 H, m); MS *m/z* (relative intensity) 320 (M^+, 12), 277 (4), 178 ($[M - PhSO_2H]^+$, 22), 151 (100); mass found *m/z* 320.1447, calcd for $C_{18}H_{24}O_3S$ (M) 320.1445. **20**: colorless oil; IR (neat) 1310, 1150; ^{1}H NMR δ 1.32 (3 H, d, *J* = 1 Hz), 1.6–2.0 (4 H, m), 2.42 (1 H, d, *J* = 5 Hz), 2.76 (1 H, dd, *J* = 5, 1 Hz), 3.14 (2 H, m), 3.7–4.1 (4 H, m), 7.4–8.0 (5 H, m); MS *m/z* 255 ($[M - C_3H_5O]^+$, 100).

Cyclized Products 21–24. **21**: colorless oil (diastereomeric mixture with respect to the *tert*-butyl group); IR (neat) 3500 (OH), 1310, 1150; ^{1}H NMR δ 0.88, 0.90 (9 H, each s), 1.0–2.3 (12 H, m), 3.4–4.2 (5 H, m), 7.4–8.0 (5 H, m); MS *m/z* (relative intensity) 408 (M^+, trace), 375 (1), 344 (2), 267 ($[M - PhSO_2]^+$, 13), 86 (100). **22**: colorless crystals; mp 177–178 °C (AcOEt–hexane); IR (KBr) 3500 (OH), 1305, 1150; ^{1}H NMR δ 1.0–2.3 (15 H, m), 2.30–2.56 (1 H, m), 3.36–3.64 (1 H, m), 3.66–4.26 (4 H, m), 7.4–8.0 (5 H, m); MS *m/z* (relative intensity) 349 ($[M - OH]^+$, trace), 224 ($[M - PhSO_2H]^+$, 5), 86 (100). Anal. Calcd for $C_{19}H_{26}O_5S$: C, 62.27; H, 7.15; S, 8.75. Found: C, 61.62; H, 7.12; S, 8.50. **23**: colorless oil; IR (neat) 3520 (OH), 1650, 1300, 1150; ^{1}H NMR δ 0.8–2.6 (16 H, m), 3.50–3.84 (1 H, m), 4.95 (1 H, s), 5.01 (1 H, s), 7.4–8.0 (5 H, m); MS *m/z* (relative intensity) 320 (M^+, 3), 302 ($[M - H_2O]^+$, 2), 179 ($[M - PhSO_2H]^+$, 100); mass found *m/z* 320.1436, calcd for $C_{18}H_{24}O_3S$ (M) 320.1444. **24**: colorless oil; IR (neat) 3510 (OH), 1300, 1175, 1150; ^{1}H NMR δ 1.15 (3 H, s), 1.4–2.2 (7 H, m), 3.1–3.6 (1 H, m), 3.7–4.0 (4 H, m), 7.4–7.9 (5 H, m); MS *m/z* (relative intensity) 170 ($[M - PhSO_2H]^+$, 11), 86 (100).

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Supplementary Material Available: ^{1}H NMR spectra of compounds **6–8**, **12–14**, **17–21**, **23**, and **24** (13 pages). Ordering information is given on any current masthead page.