68069-46-5; (−)-**7**, 87507-35-5; (±)-**8**, 87507-36-6; (+)-**8**, 87507-37-7; (−)-**8**, 68024-12-4; (±)-**9**, 87451-48-7; (+)-**9**, 87507-38-8; (−)-**9**, 87507-62-8; (±)-**11**, 77341-13-0; (±)-*anti*-**12**, 87507-39-9; (+)-*anti*-**12**, 87507-40-2; (−)-*anti*-**12**, 87507-41-3; (±)-**13**, 77341-20-9; (±)-**15**, 87507-42-4; *endo*-**15**-(*R*)-ol, 87507-60-6; *endo*-**15**-(*S*)-ol, 87507-61-7; (+)-*endo*-PNB-**15**, 87451-49-8; (−)-*endo*-PNB-**15**, 87507-43-5; (±)-*exo*-**16**, 87507-44-6; (−)-*exo*-**16**, 87507-45-7; (−)-*exo*-PNB-**16**, 87507-59-3; (±)-*endo*-**17**, 87507-46-8; (+)-*endo*-**17**, 87507-48-0; (−)-*endo*-**17**, 87507-47-9; (±)-*exo*-**18**, 87507-49-1; (±)-*endo*-**19**, 87451-50-1; (−)-*endo*-**19**, 87507-50-4; (±)-*exo*-**20**, 87507-51-5; (±)-*endo*-**21**, 87451-51-2; (+)-*endo*-**21**, 87507-63-9; (−)-*endo*-**21**, 87507-52-6; (±)-*exo*-**22**, 87507-53-7; (+)-*exo*-**22**, 87507-54-8; (±)-*endo*-**23**, 87507-55-9; (±)-**24**, 87507-56-0; (±)-**25**, 87507-57-1; (±)-*endo*-**26**, 87507-58-2; (±)-*endo*-**27**, 87451-52-3; (±)-*endo*-**28**, 87451-53-4; (±)-*endo*-**29**, 87451-54-5; (±)-*endo*-**30**, 87451-55-6; (±)-*endo*-**31**, 87451-56-7; (±)-*endo*-**32**, 87451-57-8; (±)-*endo*-**33**, 87451-58-9; (±)-*endo*-**35**, 87451-59-0; (+)-*endo*-**36**, 87451-60-3; HLADH, 9031-72-5.

Preparation and Stereochemistry of Methylation of Some Cycloalkyl Sulfones

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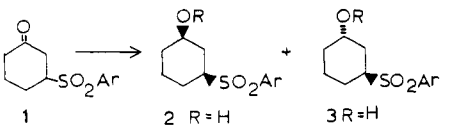
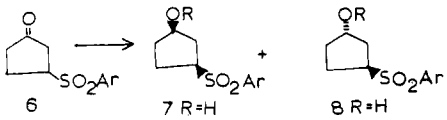
3-((4-Methylphenyl)sulfonyl)cyclohexanols (**2**, **3**), 3-((4-methylphenyl)sulfonyl)cyclopentanols (**7**, **8**), and 2-((4-methylphenyl)sulfonyl)cyclopentanols (**12**, **15**) and their tetrahydropyranyl ether derivatives were prepared. Attempted methylation of the tetrahydropyranyl ether derivatives of 2-((4-methylphenyl)sulfonyl)cyclopentanols (**13**, **16**) gave only products resulting from elimination. Methylation of the other compounds showed that cis and trans isomers generated a common set of interconverting anionic intermediates. The most stable configuration of the anion is the species that is predominantly and in some cases exclusively methylated.

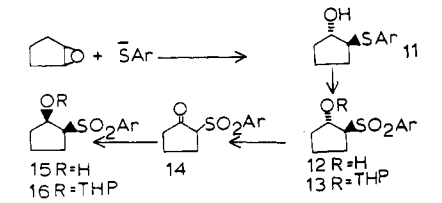
There has been much work involving α-sulfonylcarbanions. It is known that proton exchanges using a basic catalyst can occur with retention of configuration.[1-3] There have been attempts to explain the nature of stabilization and the stereochemistry of α-sulfonylcarbanions.[1-5] However, there appears to be little experimental work dealing with the stereochemistry involved in the alkylation of α-sulfonylcarbanions. We investigated the stereochemistry involved in the methylation of 1,2- and 1,3-sulfonylcyclopentanols, their tetrahydropyranyl ether derivatives,and the tetrahydropyranyl ether derivatives of 1,3-sulfonylcyclohexanols.

3-((4-Methylphenyl)sulfonyl)cyclohexanols were prepared in the following manner. 3-((4-Methylphenyl)-sulfonyl)cyclohexanone (**1**) treated with lithium aluminium



hydride led to 87% cis alcohol (**2**) and 13% of the trans isomer (**3**). Treatment of this ketone with L-Selectride (Aldrich) led to 87% of the trans and 13% of the cis alcohol. This behavior is similar to that found for the reduction of 3-*tert*-butylcyclohexanone and was of aid in assigning configuration. Reduction of 3-*tert*-butylcyclohexanone with lithium aluminum hydride gives 15% trans and 85% cis alcohols.[6] Reduction with the highly hindered lithium perhydro-9b-boraphenalyl hydride gives 72% *trans*- and 28% *cis*-*tert*-butylcyclohexanols.[6] The 3-((4-methylphenyl)sulfonyl)cyclopentanols were prepared in a similar manner. Reduction of 3-((4-methylphenyl)-sulfonyl)cyclopentanone (**6**) with lithium aluminum hydride led to 63% of *cis*- and 37% *trans*-3-((4-methylphenyl)sulfonyl)cyclopentanols (**7**, **8**). This is very similar to results reported by Richer and Gilardeau[7] for the reduction of 3-*tert*-butylcyclopentanone. Treatment of this ketone with lithium aluminum hydride led to 60% of the cis and 40% of the trans alcohols. The 1,2-sulfonylcyclopentanols were prepared as follows.





Treatment of **11** with *m*-chloroperoxybenzoic acid gave sulfone **12**. Treatment of **12** with chromium trioxide gave ketone **14** and reduction with L-Selectride gave exclusively cis alcohol **15**.

In all cases, in both the cyclopentyl and cyclohexyl sulfones, conversion of the alcohol into a tetrahydropyranyl ether derivative and subsequent regeneration of the alcohol did not lead to epimerization. The NMR spectra of all

(1) (a) Cram, D. J.; Scott, D. A.; Nielsen, W. D. *J. Am. Chem. Soc.* **1961**, *83*, 3696. (b) Cram, D. J.; Whitney, T. A. *Ibid*, **1967**, *89*, 4651. (c) Cram, D. J.; Nielsen, W. D.; Rickborn, B. *Ibid.* **1960**, *82*, 6415.

(2) Maccagnani, G.; Montanari, F.; Taddei, F. *J. Chem. Soc. B* **1968**, 453.

(3) Block, E. "Reactions of Organosulfur Compounds"; Academic Press: New York, **1978**; pp 8–26, 36–56.

(4) (a) Wolfe, S.; Rauk, A.; Csizmadia, I. G. *J. Am. Chem. Soc.* **1969**, *91*, 1567.

(5) Bordwell, F. G.; Vanier, N. R.; Mathew, W. S.; Henderickson, J. B.; Skipper, P. L. *J. Am. Chem. Soc.* **1975**, *97*, 7160.

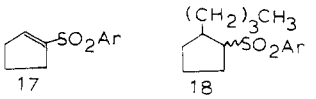
(6) Brown, H. C. "Boranes in Organic Chemistry"; Cornell University Press: Ithaca, NY, 1972; pp 243–244.

(7) Richer, J. C.; Gilardeau, C. *Can. J. Chem.* **1965**, *43*, 3419.

0022-3263/83/1948-4345$01.50/0

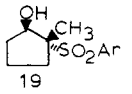
alcohols and tetrahydropyranyl ethers were compatible with the structure and were of aid in assigning and confirming configuration.

Attempted methylation of the cis-1,2-substituted cyclopentyl tetrahydropyranyl ether **16** or its trans epimer **13** by treatment with *n*-butyllithium followed by addition of iodomethane did not lead to methylated product. Instead a 59% yield of elimination[8] product **17** and a 16%



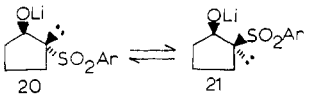
17 18

yield of **18** were isolated. Presumably **18** is the result of a Michael type of addition of *n*-butyllithium to alkene **17**. Methylation of the *cis*- and *trans*-2-(4-methylphenylsulfonyl)cyclopentanols (**15**, **12**) could be successfully carried out. Compounds **12** and **15** were each treated with 2 equiv of *n*-butyllithium to generate a dianion and then with 1 equiv of iodomethane. Only attack on the α-sulfonylcarbanion occurred. Both **12** and **15** gave exclusively **19** in 94–96% yield.



19

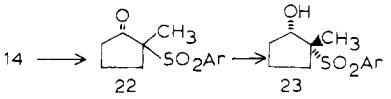
When **12** or **15** was treated with *n*-butyllithium and then quenched with water the trans alcohol **12** was isolated in 97% yield. A common intermediate is being produced from both **12** and **15**. Configuration **20** is the more stable



20 21

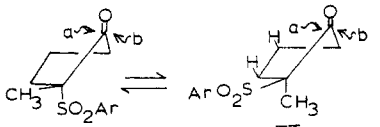
and reacts with the proton from water and also with iodomethane.

The assignment of configuration of **19** was based upon NMR comparison of the C-2 methyl and C-1 methine protons with those of its isomer **23** which was prepared as



22 23

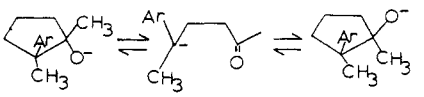
follows. Ketone **14** was methylated with sodium hydride and iodomethane and the product **22** was treated with lithium aluminum hydride. Alcohol **23** was the only isomer produced and was isolated in 79% yield. This stereoselectivity was somewhat surprising but can be rationalized. It seems possible in ketone **22** that the carbonyl dipole repels the sulfonyl oxygen dipole. This then leads to a conformation where the sulfonyl group is quasi-axial with respect to the carbonyl as shown in structure I. This could



I II

make approach of hydride by path a much easier than the alternate path b. Approach by path b could be sterically hindered by the sulfone and also by torsional interactions of the approaching hydride with the sulfone and the C-5 quasi-axial hydrogen. An alternate rationalization suggested by a referee is as follows: There could be electrostatic attraction between the sulfur and the carbonyl oxygen leading to structure II. Steric hindrance from the C-3 and C-4 hydrogens shown may block approach from the a side of structure II. This also would lead to compound **23**. At the present time we have no evidence to exclude either of these possibilities. In **19** the methyl is at δ 1.27 and the methine hydrogen is at δ 4.79 while **23** had the methyl at 1.15 and the methine hydrogen at δ 4.02. The syn hydroxyl is deshielding the methyl and the syn sulfonyl group is deshielding the methine proton in **19**. This very closely resembles the behavior found in **12** and **15**.

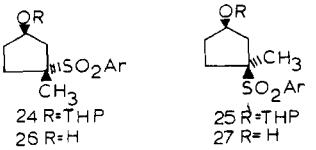
It was recognized that there may be equilibration of the cis and trans isomers **12** and **15** before dicarbanion formation and also the products may epimerize. For example, Cram and Hoffman[9] studied the base-catalyzed epimerization below. We checked for this type of ring opening



in both starting materials and products. We treated separately solutions of **12**, **15**, **19**, and **23** with 1 equiv of *n*-butyllithium and reisolated them. The starting materials were obtained in approximately 90% yield in each case with no indication of isomerization.

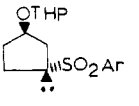
Interestingly, treatment of **12** with 2 equiv of the Grignard reagent *n*-butylmagnesium bromide followed by 1 equiv of iodomethane led to no methylated product. Instead elimination occurred to give alkene **17** in 51% isolated yield. The leaving group ability of –OMgBr is better than that of –OLi.[10]

Treatment of separate tetrahydrofuran solutions of 1,3-tetrahydropyranyloxycyclopentyl sulfones **9** and **10** with 1 equiv of *n*-butyllithium followed by iodomethane led to a 65–68% yield of methylated product. In each case the product contained 80–82% of **24** and 18–20% of **25**.



24 R=THP 25 R=THP
26 R=H 27 R=H

The isomeric distribution was determined after removal of the ether group to yield **26** and **27**. NMR integration of the C-3 methyl singlet and the methine proton was carried out. The most stable configuration of the carbanion probably has the sulfone and the tetrahydropyranyloxy group trans to each other as shown in **28**. This



28

seems probable since it has been reported that *trans*-3-alkylcyclopentanols are more stable than their cis isomers.[7,11] Anion **28** is the major intermediate being methylated.

Treatment of *cis*- and *trans*-1,3-sulfonylcyclopentanols **7** and **8** with 2 equiv of *n*-butyllithium followed by 1 equiv of iodomethane led to an 89–91% yield of methylated product with attack exclusively on the C-3 carbon atom. The product contained 48–51% of **26** and 48–51% of **27**.

(8) (a) Bosworth, N.; Magnus, P. D. *J. Chem. Soc., Perkin Trans.* 1 **1973**, 2319. (b) Magnus, P. D. *Tetrahedron* **1977**, *33*, 2024.

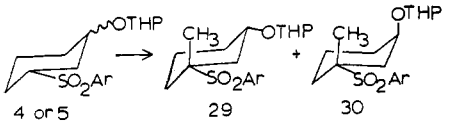
(9) Hoffman, T. D.; Cram, D. J. *J. Am. Chem. Soc.* **1969**, *91*, 1009.

(10) Pascali, V.; Tangari, N.; Umani-Ronchi, A. *J. Chem. Soc., Perkin Trans. 1* **1973**, 1166.

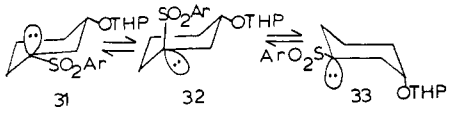
(11) (a) Fuchs, B.; Haber, R. G. *Tetrahedron Lett.* **1966**, 1447. (b) Fuchs, B.; Haber, R. G., *Ibid.* **1966**, 1323.

It seems reasonable that the steric interactions of the $-O^-$ are less severe than those of the tetrahydropyranyl ether group of **28**. Consequently, there may be only a small energy difference between cis and trans configurations of the dianion. As a result both are present and methylated essentially equally. Equilibration of the product is not taking place. When **26** or **27** was treated with *n*-butyllithium only starting material was recovered in greater than 90% yield in each case.

1,3-Tetrahydropyranyloxycyclohexylsulfones **4** and **5** were methylated in 82–88% yield and subsequently converted to alcohols. Each gave 80% of **29** and 20% of **30**.



It seems reasonable that the most stable configuration of the carbanion would be structure **31** which would have the



tolylsulfonyl cis to the tetrahydropyranyloxy group. Methylation of **31** leads to the major product **29**.

In summary, in all cases both cis and trans isomers generate a common set of interconverting anionic intermediates. The stereochemistry of the product seems to be largely controlled by the relative stability of the two configurations of the anion. The most stable configuration of the anion is the species that is predominantly methylated.

Experimental Section

Melting points were determined in capillary tubes in a Thomas-Hoover apparatus and are uncorrected. NMR spectra were run on a Jeol PSFT-100 instrument using deuteriochloroform as the solvent with tetramethylsilane as internal standard. Satisfactory elemental analyses were obtained on all new compounds and were submitted for review.

Preparation of *cis*- and *trans*-3-((4-Methylphenyl)sulfonyl)cyclohexanols (2, 3). 3-((4-Methylphenyl)sulfonyl)-cyclohexanone (1)[12] was dissolved in tetrahydrofuran, cooled to 0 °C, and treated with excess lithium aluminum hydride. After workup an 80% yield of crude product was obtained. Two components could be seen by TLC. Separation by preparative TLC on silica gel plates gave 87% of the cis isomer **2** and 13% of the trans isomer **3**. Separation by column chromatography on Florisil was also carried out to obtain larger amounts. Both isomers were recrystallized from ethyl ether–petroleum ether.

Cis isomer **2**: mp 88–90 °C; IR (CCl_4) 3600–3500, 1600, 1310, 1300, 1285, 1140 cm^{-1}; ^1H NMR δ 7.58 (4 H, center AB quartet, J = 8 Hz), 3.66 (1 H, m), 2.90 (1 H, m), 2.45 (3 H, s), 2.2–1.0 (8 H, m).

Trans isomer **3**: mp 109–111 °C; IR (CCl_4) 3600–3500, 1600, 1310, 1300, 1285, 1140 cm^{-1}; ^1H NMR δ 7.58 (4 H, center AB quartet, J = 8 Hz), 4.24 (1 H, m), 3.40 (1 H, m) 2.45 (3 H, s), 2.2–1.3 (8 H, m).

3-((4-Methylphenyl)sulfonyl)cyclopentanone (6). 2-Cyclopentenone (10.0 g, 0.121 mmol) in acetonitrile was treated with freshly prepared *p*-toluenesulfinic acid (30.0 g, 192 mmol)[13] utilizing essentially the procedure of Henry and Moore[12] to give 26.0 g (90%) of crude product as an oil. Crystallization of this material in ethyl ether gave an analytical sample: mp 73–74.5 °C; IR (CCl_4) 1760, 1608, 1500, 1460, 1310, 1295, 1285, 1145, 1090 cm^{-1}; ^1H NMR δ 7.58 (4 H, center AB quartet, J = 8 Hz), 3.77 (1 H, m), 2.47 (3 H, s), 2.65–1.70 (6 H, complex m).

***cis*- and *trans*-3-((4-Methylphenyl)sulfonyl)cyclopentanols (7, 8).** Compound **6** was dissolved in tetrahydrofuran, reacted with lithium aluminum hydride at −20 °C for 3 h, and then worked up in the usual way to give a crude product as an oil (62%). TLC examination showed two products and NMR examination showed 63% cis isomer **7** and 37% of trans isomer **8**. The compounds were separated by column chromatography on Florisil.

7: IR (film) 3500, 1600, 1500, 1450, 1315, 1302, 1288, 1145 cm^{-1}; ^1H NMR δ 7.55 (4 H, center AB quartet, J = 8 Hz), 4.29 (1 H, m), 3.57 (1 H, m), 2.46 (3 H, s), 2.30–1.85 (6 H, m).

8: IR 3500, 1600, 1500, 1450, 1315, 1302, 1288, 1145 cm^{-1}; ^1H NMR δ 7.56 (4 H, center AB quartet, J = 8 Hz), 4.49 (1 H, br s), 3.76 (1 H, m), 2.45 (3 H, s), 2.20–1.70 (6 H, m).

3-Methyl-3-((4-methylphenyl)sulfonyl)cyclopentanone (34). 3-Methyl-2-cyclopentenone in acetonitrile was treated with *p*-toluenesulfinic acid[12,13] for 48 h and then worked up and recrystallized from ethyl ether to give a 79% yield of **34**: mp 76–77 °C; IR (CCl_4) 1750, 1600, 1490, 1450; 1310, 1300, 1285, 1140 cm^{-1}; ^1H NMR δ 7.57 (4 H, center AB quartet, J = 8 Hz), 3.11–2.30 (2 H, m), 2.47 (3 H, s), 2.20–1.80 (4 H, m).

***c*- and *t*-3-Methyl-3-((4-methylphenyl)sulfonyl)-*r*-1-cyclopentanols (26, 27).**[14] Ketone **34** was dissolved in tetrahydrofuran cooled to 0 °C, excess lithium aluminum hydride was added, and the reaction was allowed to stir at 0 °C for 2 h. The reaction was worked up in the usual way to give a 90% yield of crude product as an oil. TLC examination showed two spots. NMR integration showed 83% of **27** and 17% of **26**. The two compounds were separated by chromatography on Florisil.

26: IR (film) 3500, 1600, 1500, 1450, 1310, 1300, 1285, 1150 cm^{-1}; ^1H NMR δ 7.55 (4 H, center AB quartet, J = 8 Hz), 4.47 (1 H, m), 2.80–2.60 (2 H, complex m), 2.45 (3 H, s), 1.90–1.60 (4 H, m), 1.48 (3 H, s).

27: IR (film) 3500, 1600, 1495, 1460, 1310, 1300, 1285, 1140 cm^{-1}; ^1H NMR δ 7.57 (4 H, center AB quartet, J = 8 Hz), 4.33 (1 H, m), 2.70–2.50 (2 H, m), 2.46 (3 H, s), 2.00–1.50 (4 H, m), 1.36 (3 H, s).

3-Methyl-3-((4-methylphenyl)sulfonyl)cyclohexanone (35).[15] 3-Methyl-2-cyclohexenone in acetonitrile was treated with excess *p*-toluenesulfinic acid for 48 h and the reaction was then worked up in the usual way. After recrystallization from ethyl ether a 98% yield of an analytical sample of **35** was obtained: mp 91–92 °C; IR (CCl_4) 1750, 1315, 1305, 1295, 1150 cm^{-1}; ^1H NMR δ 7.55 (4 H, center AB quartet, J = 8 Hz), 2.46 (3 H, s), 2.00–1.60 (4 H, m), 1.24 (3 H, s).

***c*- and *t*-3-Methyl-3-((4-methylphenyl)sulfonyl)-*r*-1-cyclohexanols (36, 37).** Compound **35** was dissolved in tetrahydrofuran, treated with excess lithium aluminum hydride at −78 °C, and then worked up in the usual way to give a 92% yield of crude product. TLC showed two components and NMR examination indicated a 57:43 ratio of **36** and **37**, respectively. The two isomers were separated by chromatography on Florisil.

36: mp 110–111 °C; IR 3400, 1600, 1490, 1440, 1300, 1290, 1280, 1135 cm^{-1}; ^1H NMR δ 7.53 (4 H, center AB quartet, J = 8 Hz), 4.33 (1 H, m), 2.44 (3 H, s), 2.35–1.50 (8 H, m), 1.39 (3 H, s).

37: mp 152–153 °C: IR (CCl_4) 3400, 1600, 1450, 1440, 1315, 1300, 1294, 1140 cm^{-1}; ^1H NMR δ 7.55 (4 H, center AB quartet, J = 8 Hz), 3.69 (1 H, m), 2.47 (3 H, s), 1.90–1.40 (8 H, m) 1.32 (3 H, s).

***trans*-2-((4-Methylphenyl)sulfonyl)cyclopentanol (12).** Sodium (8.20 g) was dissolved slowly in absolute ethanol and *p*-toluenethiol (44.2 g, 356 mmol) was added with stirring. Cyclopentene oxide (26.0 g, 309 mmol) was added and the mixture refluxed for 1 h under a static pressure of nitrogen. The reaction mixture was worked up in the usual way and after rotary evaporation of solvent 54.0 g of crude thioether as an oil was obtained. This was distilled, bp 185–190 °C (1 mm), 19.0 g (91.4 mmol) of the thioether was dissolved in carbon tetrachloride, and *m*-chloroperoxybenzoic acid (44.3 g, 85% pure) was added at 0 °C.

(12) Henry, R. A.; Moore, D. W. *J. Org. Chem.* **1967**, *32*, 4145.
(13) Gilman, H.; Blatt, A. H. "Organic Syntheses"; Wiley: New York, **1964**; Collect. Vol. I, p 493.
(14) We are using the nomenclature described in: "Nomenclature of Organic Compounds"; Fletcher, J. H.; Dermer, O. C.; Fox, R. B.; Eds.; American Chemical Society: Washington, DC, **1974**; Adv. Chem. Ser. No. 126, pp 112, 113.
(15) Sato, T.; Homma, I. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 1885.

The reaction was allowed to come to room temperature, stirred for 5 h, and then washed with 10% aqueous sodium sulfite until the aqueous portion was inactive to potassium iodide–starch test paper. This was worked up in the usual way to yield a white solid (20.8 g, 95%), mp 74–75 °C, as the crude product. An analytical sample was obtained by recrystallization from ether–petroleum ether: mp 74.5–75 °C; IR (CCl_4) 3500, 2980, 2890, 1600, 1450, 1320, 1305, 1290, 1150, 1090 cm^{-1}; ^1H NMR δ 7.60 (4 H, center AB quartet, J = 8 Hz), 4.45 (1 H, m), 3.32 (1 H, m), 2.45 (3 H, s), 1.98–1.70 (6 H, m).

2-((4-Methylphenyl)sulfonyl)cyclopentanone (14). Compound **12** (0.854 g, 3.56 mmol) was dissolved in acetone and cooled to 0 °C, Jones reagent, prepared from 10 g of chromium trioxide, 8.7 mL of sulfuric acid, and 30 mL of water, was slowly added until the solution remained orange, and the mixture stirred for 2 h at room temperature. The reaction mixture was worked up in the usual way and passed through a short-path silica gel column to give 0.78 g (91%) of product as an oil: IR (film) 2980, 1755, 1605, 1500, 1455, 1325, 1310, 1295, 1150, 1085 cm^{-1}; ^1H NMR δ 7.56 (4 H, center AB quartet), 3.73 (1 H, t, J = 7 Hz), 2.46 (3 H, s), 2.38–1.93 (6 H, m).

***cis*-2-((4-Methylphenyl)sulfonyl)cyclopentanol (15).** To a solution of ketone **14** (10.,5 g, 44.1 mmol) in tetrahydrofuran at −78 °C was slowly added 80 mL of 1 M L-Selectride with a syringe. The mixture was stirred under nitrogen at −78 °C for 2 h and then allowed to come to room temperature and stirred for 18 h. Water was carefully added, and then 60 mL of a 1:1 mixture of 30% hydrogen peroxide and 10% sodium hydroxide was added maintaining the temperature at 25 °C. This was stirred for 3 h and then worked up in the usual way and passed through a short path silica gel column to give 4.07 g of crude alcohol. This was recrystallized in ether–petroleum ether: mp 67–68 °C; IR (CCl_4) 3500, 2960, 2890, 1605, 1500, 1455, 1320, 1300, 1290, 1150, 1090 cm^{-1}; ^1H NMR δ 7.59 (4 H, center AB quartet, J = 8 Hz), 4.40 (1 H, m), 3.36–3.14 (1 H, m), 2.46 (3 H, s), 2.30–1.90 (7 H, m).

Attempted Methylation of 2-[*trans*-2-(4-Methylphenylsulfonyl)cyclopentyloxy]oxacyclohexane (13). Tetrahydropyranyl ether **13** was dissolved in 10 mL of tetrahydrofuran and cooled to −78 °C under nitrogen n-butyllithium (2.3 M, 1.55 mL, 3.65 mmol) was added, the solution was stirred for 15 min, and then 10.23 mL (3.65 mmol, of iodomethane was added. After 3 h of stirring at −78 °C the reaction mixture was worked up in the usual way. Removal of the solvent under reduced pressure gave an oil, 0.828 g. The NMR spectrum of this oil showed no methyl singlet. TLC showed two major products. Silica gel chromatography gave 0.422 g (59%) of 1-((4-methylphenyl)sulfonyl)-cyclopentene (**17**) as white crystals and 0.141 g (16%) of 1-n-butyl-2-((4-methylphenyl)sulfonyl)cyclopentane (**18**) as an oil.

17: mp 95–97 °C; IR (CCl_4) 3095, 2910, 1620, 1600, 1500, 1445, 1320, 1310, 1290, 1150 cm^{-1}; ^1H NMR δ 7.55 (4 H, center AB quartet, J = 8 Hz), 6.71 (1 H, s), 2.54–2.47 (4 H, m), 2.44 (3 H, s) 2.01 (2 H, m); MS, m/e (relative intensity) 222 (20, M^+), 139 (100).

18: IR (film) 2970, 2880, 1600, 1500, 1455, 1310, 1300, 1290, 1145, 1090 cm^{-1}; ^1H NMR δ 7.55 (4 H, center AB quartet, J = 8 Hz), 3.02 (1 H, m), 2.44 (3 H, s), 1.60–1.25 (13 H, m), 0.81 (3 H, t, J = 7 Hz); MS, m/e (relative intensity) 280 (1, M^+), 125 (50), 91 (10), 69 (100).

Methylation of *cis*- or *trans*-2-((4-Methylphenyl)-sulfonyl)cyclopentanol. To a solution of **12** or **15** (371 mg, 1.54 mmol) in tetrahydrofuran at −78 °C under a nitrogen cover was added 1.41 mL of n-butyllithium (2.3 M, 3.24 mmol). The mixture was stirred at −78 °C for 10 min and 0.105 mL of iodomethane (1.69 mmol) was added. The reaction was stirred for 4 h at −78 °C and then worked up as usual to yield 0.381 g (98%) of crude c-2-methyl-2-((4-methylphenyl)sulfonyl)-r-1-cyclopentanol (**19**),[14] which was purified by column chromatography on Florisil and subsequent recrystallization from ether–hexane: mp 78.5–81 °C; IR (CCl_4) 3500, 2980, 2890, 1605, 1500, 1445, 1310, 1305, 1290, 1145, 1090 cm^{-1}; ^1H NMR δ 7.75 (4 H, center AB quartet, J = 8 Hz), 4.79 (1 H, m), 2.46 (3 H, s), 2.2–1.6 (6 H, m), 1.27 (3 H, s).

2-Methyl-2-((4-methylphenyl)sulfonyl)cyclopentanone (22). Sodium hydride (92.0 mg, 3.80 mmol) was added to a mixture of ethyl ether (5 mL) and dimethyl sulfoxide (5 mL) and stirred at 0 °C, and ketone **14** (0.557 g, 2.34 mmol) was added. The reaction was allowed to warm to room temperature, and 0.145 mL (2.34 mmol) of iodomethane was injected into the mixture and stirred for 1 h. The reaction was worked up in the usual way to give 0.525 g (89%) of crude product, mp 119–121 °C. Recrystallization from ether–petroleum ether gave an analytical sample: mp 123–124 °C; IR (CCl_4) 1752, 1600, 1500, 1460, 1320, 1310, 1291, 1145 cm^{-1}; ^1H NMR δ 7.51 (4 H, center AB quartet, J = 8 Hz), 3.00–2.45 (2 H,m), 2.45 (3 H, s), 2.10–1.70 (4 H, m), 1.31 (3 H, s).

***t*-2-Methyl-2-((4-methylphenyl)sulfonyl)-*r*-cyclopentanol (23).** Ketone **22** in THF was reduced with lithium aluminum hydride at −78 °C and worked up in the usual way to yield crude **23** in 80% yield, mp 85–89 °C. Recrystallization from ether–hexane gave an analytical sample: mp 92–93 °C; IR (CCl_4) 3500, 1600, 1500, 1450, 1315, 1300, 1280, 1140, 1080, 1040 cm^{-1}; ^1H NMR δ 7.59 (4 H, center AB quartet, J = 8 Hz), 4.02 (1 H, m), 2.46 (3 H, s), 1.15 (3 H, s), 2.00–1.60 (6 H, m).

General Procedures. All methylations were carried out by using essentially the procedure described for **12** and **15** using 2 equiv of n-butyllithium and 1 of iodomethane for all alcohols and 1 equiv of n-butyllithium and 1 equiv of iodomethane for tetrahydropyranyl ethers.

All tetrahydropyranyl ethers were prepared using standard techniques. The alcohols were regenerated from these ethers also using standard tecniques.

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