charge-transfer (MLCT) absorptions of the $Co(bzo_3[12]hexaeneN_3)_2^{2+}$ complexes occur at relatively low energies (λ_{max} = 570 and 550 nm, respectively), and the comparisons may be complicated by inter- or intramolecular MLCT perturbations.

Similarly, the much larger value of β estimated for $Co(Me_4[14]tetraeneN_4)(NH_3)_2^{3+}$ than for $Co([14]aneN_4)(NH_3)_2^{3+}$ is very likely a consequence of the low-energy π^* acceptor system of the tetraene ligand and the resulting MLCT perturbations. It seems likely that charge-transfer perturbations contribute to donor-acceptor electronic coupling (i.e., H_{RP}) in most experimental systems and that it is very difficult to design experiments which provide information about charge-transfer independent contributions to H_{RP}. Nevertheless, neither charge-transfer perturbations nor variations in size can contribute significantly to the variations of β_{ab} in Figure 2.

Conclusions

In this study we have documented some systematic deviations from predictions of the Marcus square-root relation of a series of Co(III)-Co(II) electron-transfer reactions. The magnitudes of the discrepancies have been found to correlate with the mismatch of the energies of the lowest energy ligand field excited states of the reactant and product Co(III) and Co(II) species. This effect appears to be qualitatively consistent with either (or both) (a) a larger value of the one-electron exchange integral when the reactants and products are electronically degenerate (i.e., a "pure" electronic effect) or (b) a modulation in the electronic wave function by the variations in nuclear coordinates across the reaction trajectory (i.e., a vibronic effect). A vibronic effect is likely to be manifested, at least partly, by changes in enthalpies of activation.

Self-exchange electron transfer-reactions define the electronically degenerate limit in which electron-transfer behavior becomes relatively adiabatic. Our experimental probes necessarily provide only relative information and do not permit any inference about the degree to which the self-exchange reactions themselves might be nonadiabatic.

The effects that we have investigated do appear to be electronic in origin, and the magnitude of their kinetic manifestations can be altered by simple electronic perturbations. Despite the contributions of these electronic effects to electron-transfer reactivity patterns, it is important to bear in mind that the dominant factors in these reactions are clearly those associated with nuclear reorganization and that these factors do seem to be adequately treated by using various quantum, semiclassical, or classical models. Indeed, it is only the systematic deviations from predictions of such models that permit the identification of electronic factors.

The major conclusion of this study, that electron-transfer reactions tend to become less adiabatic as the electronic structures of reactants and products become more dissimilar, has been demonstrated for a somewhat unique set of reactions: i.e., these involving Co(III) oxidants and Co(II) reductants. An approximate selection rule governing the adiabaticity of these reactions can be given an "electronic" or a "vibronic" formulation. Thus, mismatched electronic excited states of reactants and products will lead to retardation of electron-transfer rates (a) when at least one of the electron-density functions in the exchange integral (e.g., ρ^{III} or ρ^{II} in eq 3) is very small (as when the oxidized species of the reactants and products both have filled redox orbitals) and (b) the first coordination sphere nuclear reorganization contributions are large and when the electronic wave functions for the redox orbitals of both the oxidant and reductant contain significant contributions from distorted electronic excited states. Further study may permit a more precise statement of the electronic selection rules governing electron-transfer processes.

Stereochemistry of Allyl Sulfones. On the Structure of Metalated Allyl Sulfones and Their Stereochemistry of Alkylation

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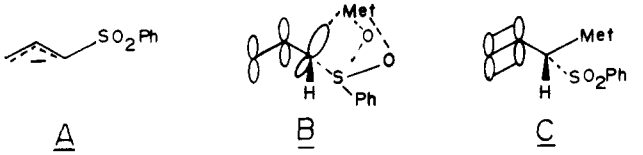
Abstract: Stereochemical studies involving alkylation of metalated allyl sulfones are probed to address the question of the structure of these important synthetic intermediates. In contrast to recent conclusions, both experimental and theoretical, declaring sulfone-stabilized carbanions planar, the diastereoselectivity of these alkylations questions such conclusions even though the additional allylic conjugation would have been anticipated to provide a further driving force for planarity. A model to rationalize the seemingly contrasteric highly diastereoselective alkylations in which the sulfone-stabilized allylic carbanion exists as a somewhat pyramidalized organometallic emerges. The preferred conformations of the cyclohexenyl allylic sulfones place the sulfone moiety in an axial orientation and, in at least one acyclic case, the C-S bond parallel to the p-orbitals. An electronic stabilization is proposed to account for this conformation. In addition, the stereochemistry of the palladium-catalyzed allylic alkylation with arylsulfinate places this nucleophile into the class of heteroatom nucleophiles that proceed with predominant net retention of configuration.

The question of the nature of a carbanion stabilized by a sulfone group continues to be a major controversy. While evidence has accumulated to suggest that such carbanions behave asymmetrically,[1] recent experimental[2a] and theoretical[2b] work has pronounced them planar. Intuition would lead one to predict that conjugating a sulfone stabilized carbanion with a double bond as in the case of carbanions derived from allylsulfones should indeed assure their planarity as in A. We wish to record evidence that



A B C

questions the validity of such conclusions for metalated allyl sulfones. Structures such as B or C differ only in the degree of

(1) For reviews, see: Durst, T. *Compr. Org. Chem.* **1979**, *3*, 171-195. Magnus, P. D. *Tetrahedron* **1977**, *33*, 2019. Kocienski, P. J. *Chem. Ind. (London)* **1981**, 548. Block, E. "Reactions of Organosulfur Compounds"; Academic Press: NY, 1978; pp 50-53.

(2) (a) Lett, R.; Chassaing, G.; Marquet, A. *J. Organomet. Chem.* **1976**, *111*, C17; Bordwell, F. G.; Branea, J. C.; Johnson, C. R.; Vanier, N. R. *J. Org. Chem.* **1980**, *45*, 3884. (b) Wolfe, S.; Stolow, A.; La John, L. A. *Tetrahedron Lett.* **1983**, 4071.

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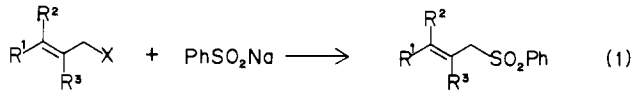
pyramidalization which, in turn, would depend upon the degree of interaction of the metal with carbon. In either case, a stereochemical bias is, of necessity, introduced.

Our interest in these fundamental questions of the structure of metalated allyl sulfones derived from the possibility of using a sulfone as a leaving group in displacement reactions for C–C bond formation.[3-5] Because the synthetic application of sulfones mainly removed the sulfone group by reduction or elimination to olefins and acetylenes,[6-8] the stereochemistry of the sulfone was virtually ignored. On the other hand, combining displacement reactions with the formation of C–C bonds via α-sulfonyl carbanions would convert a sulfone into an equivalent of a 1,1-dipole, or, in the case of an allyl sulfone, a 1,1- or 1,3-dipole.[4] For such reactions, the stereochemistry of the allyl sulfone is quite important. Thus, we embarked upon an investigation of the stereochemical consequences associated with the various methods to form allyl sulfones. The stereochemical consequences of alkylation of metalated allyl sulfones should provide some insight into the structure of these species, a most important practical as well as theoretical question for these extremely important synthetic intermediates. Indeed, the results proved to be most surprising.

Formation of C–S Bond. For the simple allylic sulfones **1–4**, the standard displacement of an allylic leaving group such as chloride or bromide with sodium benzenesulfinate sufficed (eq 1).[1,6,7] With a more sterically hindered system as in **5**, the

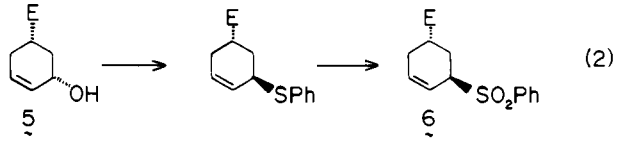


(1)

X = Cl, Br

	R^1	R^2	R^3	%
1	CH_3	H	H	73
2	H	H	CH_3	89
3	CH_3	CH_3	H	63
4	H	H	Ph	65

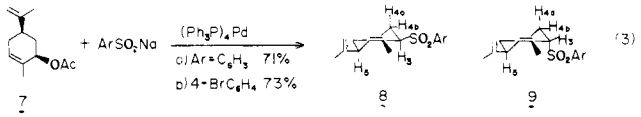
benzenesulfinate anion proved to be insufficiently reactive so that complications ensued. In this case, the methanesulfonate generated in situ was easily displaced by thiophenoxide anion. Oxidation of the resultant sulfide produced the (*E*)-sulfone **6** in 42% overall yield (see eq 2).



(2)

E = CO_2CH_3

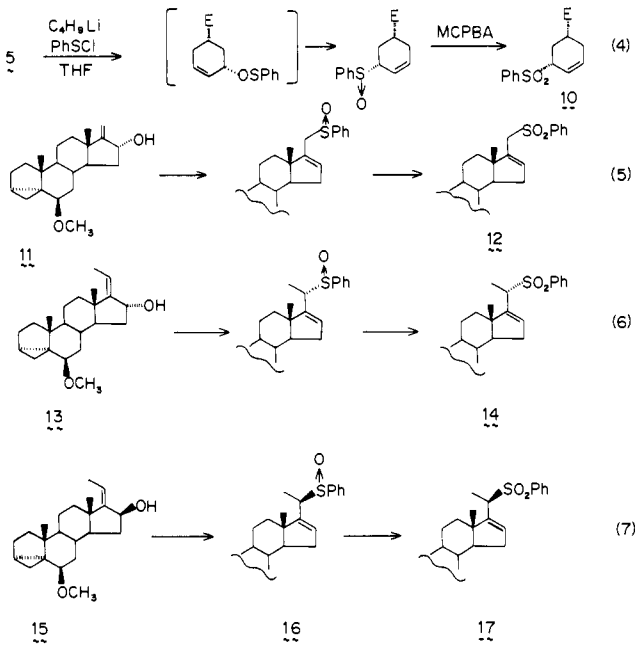
A useful method for the replacement of an allylic hydroxyl group with sulfone is the palladium-catalyzed exchange of an allylic acetate with sodium benzenesulfinate.[9] When this new method was used, the (*Z*)-acetate **7** containing 8% of the *E*-isomer formed predominantly the (*Z*)-sulfone **8** (Ar = Ph, *p*-BrC_6H_4) contaminated with 20–30% of the *E*-isomer (see eq 3). This result



(3)

places the sulfinate anion in the same class as the carboxylate[10] and amine nucleophiles[11] with respect to palladium-catalyzed allylic alkylations. While we cannot exclude totally some equilibration of **8** to **9** under the reaction conditions, the product ratio does not represent an equilibrium mixture since equilibration of **8** and **9** leads to a 1:3 ratio.

Formation of allyl sulfenates accompanied by rearrangement constitutes a stereocontrolled synthesis of allyl sulfoxides[12] and, after oxidation, of allyl sulfones as shown in eq 4–7. The reactions



(4)

(5)

(6)

(7)

of eq 4, 5,[13] and 6[13] proceeded satisfactorily to give **10**, **12**, and

(3) Parker, W. L.; Woodward, R. B. *J. Org. Chem.* **1969**, *34*, 3085. Campbell, R. V. M.; Crombie, L.; Findley, D. A. R.; King, R. W.; Pattenden, G.; Whiting, D. A. *J. Chem. Soc., Perkin Trans. 1* **1975**, 897. Same as ref 6n.

(4) For organocopper chemistry and sulfones, see: Julia, M.; Righini, A.; Verpeaux, J. N. *Tetrahedron Lett.* **1979**, 2393; *Tetrahedron* **1983**, *39*, 3283. For organonickel chemistry and sulfones, see: Cuvigny, T.; Julia, M. *J. Organomet. Chem.* **1983**, *250*, C21.

(5) For organopalladium chemistry and sulfones, see: Trost, B. M.; Schmuff, N. R.; Miller, M. J. *J. Am. Chem. Soc.* **1980**, *102*, 5979.

(6) For a few representative examples, see: (a) Julia, M.; Arnould, D. *Bull. Soc. Chim. Fr.* **1973**, *743*, 746. (b) Julia, M.; Ward, P. *Ibid.* **1973**, 3065. (c) Julia, M.; Uguen, D. *Ibid.* **1976**, 513. (d) Grieco, P. A.; Masaki, Y. *J. Org. Chem.* **1974**, *39*, 2135. (e) Grieco, P. A.; Masaki, Y.; Boxler, D. *Ibid.* **1975**, *40*, 2261. (f) Olson, G. L.; Cheung, H.-C.; Morgan, K. D.; Neukom, C.; Saucy, G. *Ibid.* **1976**, *41*, 3287. (g) Manchand, P. S.; Wong, H. S.; Blount, J. F. *Ibid.* **1978**, *43*, 4769. (h) Kocienski, P. J. *J. Org. Chem.* **1980**, *45*, 2037. (i) Janssen, C. G. M.; Godefroi, E. F. *Ibid.* **1982**, *47*, 3274. (j) Hamann, P. R.; Fuchs, P. L. *Ibid.* **1983**, *48*, 914. (k) Donaldson, R. E.; Saddler, J. C.; Byrn, S.; McKenzie, A. T.; Fuchs, P. L. *Ibid.* **1983**, *48*, 2167. (l) Fischli, A.; Mayer, H.; Simon, W. Stoller, H. J. *Helv. Chim. Acta* **1976**, *59*, 397. (m) Buddhsukh, D.; Magnus, P. D. *J. Chem. Soc., Chem. Commun.* **1975**, 952. (n) Campbell, R. V. M.; Crombie, L.; Findley, D. A. R.; King, R. W.; Pattenden, G.; Whiting, D. A. *J. Chem. Soc., Perkin Trans. 1* **1975**, 897. (o) Carr, R. V. C.; Paquette, L. A. *J. Am. Chem. Soc.* **1980**, *102*, 853. (p) Bloch, R.; Abecassis, J. *Tetrahedron Lett.* **1982**, *23*, 3277. (q) Paquette, L. A.; Kinney, W. A. *Ibid.* **1982**, *23*, 5127. (r) Woodward, R. B.; Wuonola, M. A. *Tetrahedron* **1976**, *32*, 1085.

(7) Also see: (a) Julia, M.; Uguen, D.; Callipolitis, A. *Bull. Chim. Soc. Fr.* **1976**, 519. (b) Manchand, P. S.; Rosenberger, M.; Saucy, G.; Wehrli, P. A.; Wong, H.; Chambers, L.; Ferro, M. P.; Jackson, W. *Helv. Chim. Acta* **1976**, *59*, 387. (c) Savoia, D.; Trombini, C.; Umani-Ronchi, A. *J. Chem. Soc., Perkin Trans. 1* **1977**, 123. (d) Torii, S.; Uneyama, K.; Kawahara, I. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 949. (e) Kocienski, P. J. *Tetrahedron Lett.* **1979**, 441. (f) Uneo, Y.; Aoki, S.; Okawara, M. *J. Chem. Soc., Chem. Commun.* **1980**, 683. (g) Torii, S.; Uneyama, K.; Matsunami, S. *J. Org. Chem.* **1980**, *45*, 16. (h) Lansbury, P. T.; Erwin, R. W.; Jeffrey, D. A. *J. Am. Chem. Soc.* **1980**, *102*, 1602. (i) Taber, D. F.; Saleh, S. A. *J. Org. Chem.* **1981**, *46*, 4817. (j) Moiseenkov, A. M.; Polunin, E. V.; Semenovsky, A. V. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 1057. (k) Sato, K.; Inoue, S.; Onishi, A.; Uchida, N.; Minowa, N. *J. Chem. Soc., Perkin Trans. 1* **1981**, 761. (l) Jonczyk, A.; Radwan-Pytlewski, T. *J. Org. Chem.* **1983**, *48*, 910.

(8) Hirama, M. *Tetrahedron Lett.* **1981**, *22*, 1905. Kraus, G. A.; Frazier, K. *Synth. Commun.* **1978**, *8*, 483. Vasil'eva, L. L.; Mel'nikova, V. I.; Gainullina, E. T.; Pivnitskii, K. K. *Zh. Org. Khim.* **1980**, *16*, 2618. Ueno, Y.; Ohta, M.; Okawara, M. *J. Organomet. Chem.* **1980**, *197*, C1.

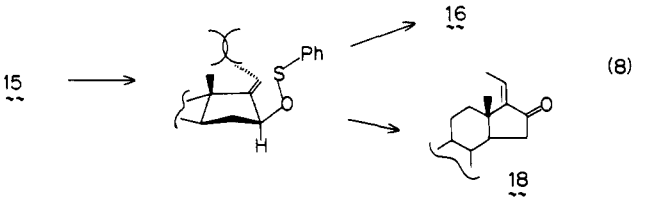
(9) At the time of our independent work, a similar observation was reported. See: Julia, M.; Nel, M.; Saussine, L. *J. Organomet. Chem.* **1979**, *181*, C17. Julia, M.; Lave, D.; Mulhauser, M.; Ramirez-Munoz, M.; Uguen, D. *Tetrahedron Lett.* **1983**, *24*, 1783. Inomata, K.; Yamamoto, T.; Kotake, H. *Chem. Lett.* **1981**, 1357.

(10) Trost, B. M.; Verhoeven, T. R.; Fortunak, J. M. *Tetrahedron Lett.* **1979**, 2301. Bäckvall, J. E.; Nordberg, R. E. *J. Am. Chem. Soc.* **1981**, *103*, 4959.

(11) Trost, B. M.; Keinan, E. *J. Am. Chem. Soc.* **1978**, *100*, 7779. Bäckvall, J. E.; Nordberg, R. E.; Nyström, J. E. *Tetrahedron Lett.* **1982**, *23*, 1617.

(12) For reviews, see: Evans, D. A.; Andrews, G. C. *Acc. Chem. Res.* **1974**, *7*, 147. Hoffman, R. W. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 563.

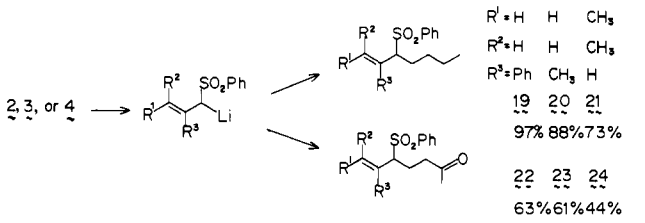
14 in 30%, 52% and 58% overall yield, whereas the overall yield of **17** was only 13%. In the case of **15**, substantial problems arose in the first step giving **16** in only 26% yield. In addition to recovered starting material (14%), a coproduct was the enone **18** which may arise by a competitive E2 elimination of the intermediate sulfenate (see eq 8). A 1,3-diaxial-like interaction in



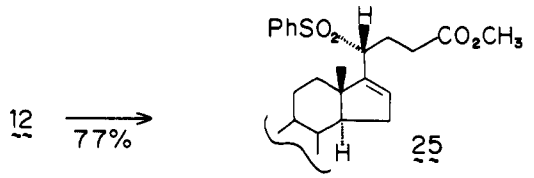
(8)

the sulfenate that arises in order to attain the required geometry for the [2,3]-sigmatropic rearrangement may be responsible for the poor yield of **16**.

Alkylation of Allyl Sulfones. In most cases, the anions were usually generated using *n*-butyllithium as base.[6,7] Alkylation with *n*-butyl iodide proceeded uneventfully in good yields.

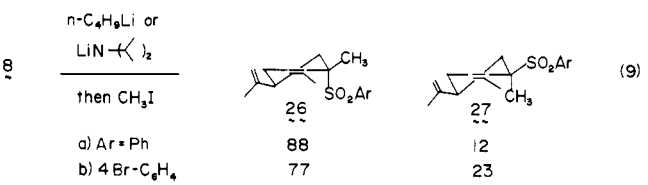


Most interestingly, addition of methyl vinyl ketone to the lithium salts in THF at −78 °C followed by quenching with methanol also proceeded well. Such aprotic Michael reactions are not so common. Allyl sulfone anions apparently are excellent Michael donors.[8] In the case of the steroid **12** using methyl acrylate as the



Michael acceptor, a protic solvent was preferred in the Michael reaction to give the product in 77% yields in a 4:1 diastereomeric ratio (only the major diastereomer is depicted). Our inability of epimerize similar sulfones under similar conditions suggests the stereochemistry is kinetically controlled. Thus, *good stereoselectivity can be achieved in such conjugate additions.*

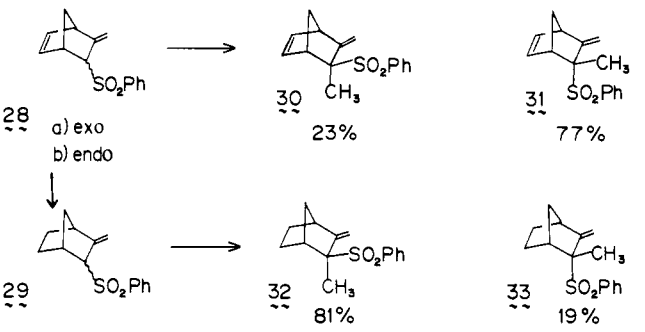
The methylation of **8** (88% yield) proved most interesting in



(9)

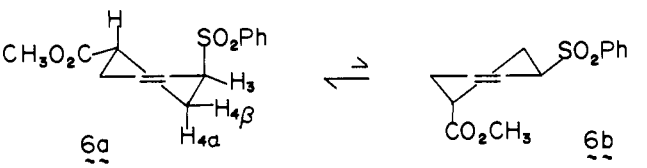
that equatorial attack predominated. Assuming a delocalized carbanion, such a result is quite surprising since a twist boat conformation of **26** would be required as an initial product in order to maintain orbital overlap.[14] The high diastereoselectivity in this reaction allows the major isomer to be obtained pure by recrystallization.

Most unusual is the complementary stereochemistry resulting from the alkylation of the two bicyclic sulfones **28**[15] and **29**.[15]



First, the stereochemistry of the alkylation is independent of the stereochemistry of the starting sulfone since either the pure exo or pure endo isomer of **28** gives the same product ratio. Second, attack on the exo face should be a priori expected.[16,17] Furthermore, the presence of the double bond of the norbornenyl system should not affect that expected preference. While the norbornenyl system fits expectation based on simple steric arguments, the norbornyl system gives predominantly endo attack—a contrasteric result. The stereoselective alkylation of allyl sulfones appears general, although the source of the selectivity is not immediately apparent.

Stereochemistry of Allyl Sulfones. The stereochemistry of **6**



is easily assigned from the NMR spectra. $J_{3,4\alpha}$ and $J_{3,4\beta}$ of 6.6 and 3.6 Hz, respectively, indicate that H(3) is mainly equatorial. These facts not only indicate the *E* stereochemistry but also suggest the preference for conformer **6a** *with an axial benzenesulfonyl group*! This conformation is verified by $J_{4\alpha,5}$ and $J_{4\beta,5}$ of 10.7 and 3.7 Hz which indicate H(5) is axial and consequently the carbomethoxy group is equatorial. This stereochemistry is that expected for a simple S_N2 displacement with inversion of configuration in contrast to a S_N2' with retention.[18]

The stereoisomer **10** shows $J_{3,4\alpha}$ and $J_{3,4\beta}$ of 11.8 and <2 Hz which indicates H(3) is axial and consequently the sulfone is equatorial. Similarly, $J_{4\alpha,5}$ and $J_{4\beta,5}$ of 13.0 and <2 indicate H(5) is axial and consequently the carbomethoxy group is also equatorial. The *Z*-stereochemistry follows from the method of preparation which, arising from a [2,3]-sigmatropic rearrangement of the allylic alcohol **5**, should give rise to the same relative stereochemistry as **5**, i.e., *Z*.

Similar arguments allow assignment of the stereochemistry of **8** and **9**. For example, in the case of **8b**, $J_{4\alpha,5}$ = 12.9 Hz establishes the axial nature of H(5) and therefore the equatorial nature of the isopropenyl group. The sulfone is also equatorial as defined by the appropriate coupling constant, $J_{3,4\alpha}$ = 10.7 Hz. The *Z* geometry is thereby established. On the other hand, in **9a** and **9b**, $J_{4\alpha,5}$ of 13.5 Hz, and and $J_{3,4\alpha}$ of 6 Hz indicates the equatorial and pseudoaxial nature of the isopropenyl and sulfone groups, respectively, and thus the *E* geometry. These coupling constants also define the preferred conformation of **9** *with the sulfonyl group axial*!

(13) For preparation of **11** and **13**, see: Schmuff, N. R.; Trost, B. M. *J. Org. Chem.* **1983**, *48*, 1404.

(14) For a few illustrations of axial bias in alkylations, see: House, H. O.; Umen, M. J. *J. Org. Chem.* **1973**, *38*, 1000. Corey, E. J.; Enders, D. *Chem. Ber.* **1978**, *111*, 1337, 1362. Lyle, R. E.; Fribush, H. M.; Lyle, G. G.; Saavedra, J. E. *J. Org. Chem.* **1978**, *43*, 1275.

(15) Veniard, L.; Benaim, J.; Pourcelot, G. *C. R. Hebd. Seances Acad. Sci., Ser. C* **1968**, *266*, 1092. Barbarella, G.; Cinquini, M.; Colonna, S. *J. Chem. Soc., Perkin Trans. 1* **1980**, 1646.

(16) Cf. Krapcho, A. P.; Dundulis, E. A. *J. Org. Chem.* **1980**, *45*, 3236. Trost, B. M.; Tamaru, Y. *J. Am. Chem. Soc.* **1977**, *99*, 3101. Bochme, W. R.; Schipper, E.; Scharpf, W. G.; Nichols, J. *Ibid.* **1958**, *80*, 5488. Eigen, M. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 1.

(17) Korvola, J. Hakli, H.; Paasivirta *J. Finn. Chem. Lett.* **1974**, *16*. Masar, S. E.; Krieger, H. *Suom. Kemistil. B* **1969**, *42*, 1. McConaghy, J. S., Jr.; Bloomfield, J. J. *J. Org. Chem.* **1968**, *33*, 3425. Barraclough, P.; Young, D. W. *Tetrahedron Lett.* **1970**, *26*, 2293. Also see: Abad, G. A.; Jindal, S. P.; Tidwell, T. T. *J. Am. Chem. Soc.* **1973**, *95*, 6326.

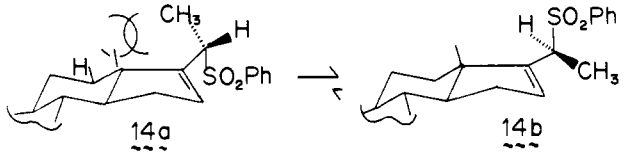
(18) Cf. Stork, G.; Kreft, A. F., III. *J. Am. Chem. Soc.* **1977**, *99*, 3850.

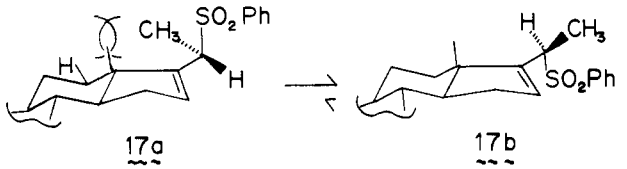
Table I. Deuterium Incorporation in **6** and **10**

entry	initial sulfone	base concn, M	time, h	product sulfone C-1[b]	product sulfone C-3[c]	product sulfone C-5[d]	**10**[e] C-1[f]	**10**[e] C-3[g]	ratio **6**/**10**
1	**6**	0.26	3.0	0	89	38	0	89	56/44
2	**6**	0.35	8.0	34	>95	100	41	>95	56/44
3	**10**	0.29	14.5	50	h	h	40	h	58/42

[a] Determined by NMR integration of the appropriate signals. [b] δ 6.14. [c] Signals for **6**, and **10**, overlapping 5.72 for **6** and 5.89 for **1**. Thus, the % deuterium incorporation is for both. [d] δ 2.94. [e] Exchange at C-5 could not be determined. [f] δ 6.03. [g] δ 2.54. [h] Not determined.

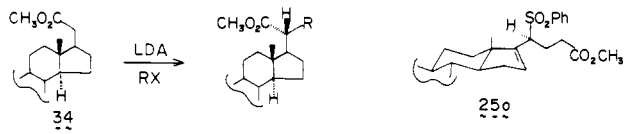
Stereochemical assignments of **14** and **17** derive from their method of preparation. The [2,3]-sigmatropic rearrangement of the intermediate sulfinate ester translates the stereochemistry of the allylic alcohol into the stereochemistry of the sulfoxides and, consequently, the sulfones. The NMR spectra show substantial differences—the most striking is the absorption for the C(18) methyl group which appears at δ 0.42 for **14** and δ 0.77 for **17**.





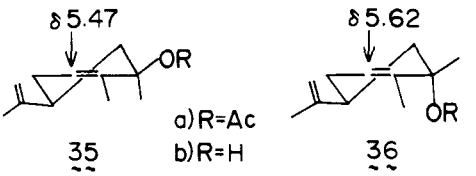
These relative shifts and the known shielding effect of a phenylsulfonyl group[19] when eclipsed with a methyl group support the conformation depicted as **14b** for **14** and **17b** for **17**. These conformations also conform to the apparent propensity of the C–SO_2Ph bond to want to align itself with the p-orbitals of the olefin. It can be seen from the drawings that these conformations further support the stereochemical assignments in that the nonbonded interactions between the side chain methyl group and C(12) of **14a** and **17a** should disfavor these conformations relative to **14b** and **17b** in agreement with our observations.

A similar analysis allows us to assign the stereochemistry depicted in **25** as the major epimer of the conjugate addition product.

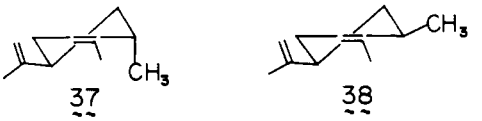


In particular, the NMR absorption for the C(18) methyl protons of the major adduct appear at δ 0.46, which agrees well with the corresponding signal of **14b**. The same absorption for the minor isomer appears at δ 0.77 which agrees well with the corresponding absorption of **17b**. On this basis, conformer **25a** may also be assigned as the preferred one. Thus, the alkylation of **12** proceeds via the same stereochemical pathway as the alkylation of **34**.[20]

The assignments of **26** and **27** derive from a comparison of their NMR spectral data to that of **8** and **9**. A detailed examination of the NMR data of the latter compounds establishes the following trends: (1) the C(10) methyl absorptions appear at *lower* field for **8** (δ 2.05) than for **9** [δ 1.98 (a) and 1.99 (b)]; (2) the ring vinyl proton absorptions appear at *higher* field for **8** [δ 5.80 (a), 5.88 (b)] than for **9** [δ 5.84 (a), 5.93 (b)]; (3) the absorption for H(5) appears at *higher* field for **8** [δ <2.2 (a), <2.1 (b)] than for **9** [δ 2.46 (a), 2.47 (b)]; (4) the geminal coupling constant for H(4) is smaller in **8** (J = 12.9 Hz) than in **9** (J = 14.5 Hz); (5) the ASIS[21] for the isopropenyl methyl group of **8** is $\Delta\delta$ = 0.23 and that of **9** is $\Delta\delta$ = 0.16. The corresponding comparisons for **26** and **27** follow the exact same trends. The C(10) methyl absorption of **27** appears at *lower* field (δ 2.08) than the one for **26** (δ 2.01). The ring vinyl proton of **27** absorbs at *higher* field [δ 5.75 (a), 5.76 (b)] than for that of **26** [δ 5.90 (a), 5.92 (b)]. This effect appears to derive from more effective overlap of the electronegative sulfone with the π-bond when it is axial rather than equatorial. Polarization of electron density away from C(1) by mixing of the π-orbital with the σ^* orbital of the C–X bond may account for this effect. A similar trend is observed with the acetates **35** and **36**[22] and may be general. The absorption of H(5)



of **27** appears at *higher* field (δ <2.20) than that of **26** [δ 2.57 (a), 2.60 (b)]. The geminal coupling constant for the C(4) methylene protons of **26** of 14.7 Hz and the ASIS of the isopropenyl methyl group of $\Delta\delta$ = 0.18 of **26** correspond to the values for **9**. Additional confirmation comes from the relative shifts of the methyl group at C(3). The general trend in these systems has been for the axial methyl group to absorb at *lower* field (**35b** δ 1.31, **37** $\delta\delta$ 1.07) than the equatorial methyl group (**36b** δ 1.29,



38 δ 0.94).[23] The same trend is observed for **27** (δ 1.62) and **26** (δ 1.50).

The assignments for **30**–**33** arise by comparison of the NMR spectral data to that of the literature. The chemical shifts of the methyl groups are diagnostic. This absorption for the exo isomers appears at *lower* field (**31** δ 1.72; **33** δ 1.50) than for the endo isomers (**30** δ 1.41; **32** δ 1.41).[15]

Equilibration. The thermodynamic ratio of stereoisomers was determined by simple base equilibration. Treatment of **8** and **9** with sodium methoxide in methanol led to a **9**:**8** ratio of 76:24 as determined by NMR integration of the vinyl proton absorptions. *Thus, the phenylsulfonyl group prefers an axial orientation!* Since such a bias might derive from an $A_{1,2}$ strain[24] due to the olefinic methyl group, **6** and **10** which lack this methyl group were also equilibrated. Here, too, the axial orientation of the sulfone group was preferred; the **6**:**10** ratio of 57:43 was determined by integration of the vinyl protons. We had previously shown that the sulfone group prefers to be axial in **6** (i.e., **6a** is preferred over **6b**, vide supra).

In the case of **6** and **10**, equilibration could occur either by deprotonation α to the sulfone or α to the ester. Previous work

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(20) Wicha, J.; Bal, K. *J. Chem. Soc., Perkin Trans. 1* **1978**, 1282; Partridge, J. J.; Shiney, S.-J.; Chadha, N. K.; Baggiolini, E. G.; Hennessey, B. M.; Uskokovic, M. R.; Napoli, J. L.; Reinhardt, T. A.; Horst, R. L. *Helv. Chim. Acta* **1981**, *64*, 2138.

(21) ASIS = aromatic solvent induced shift.

(22) Schmuff, N. R. Ph.D. thesis, University of Wisconsin, 1982.

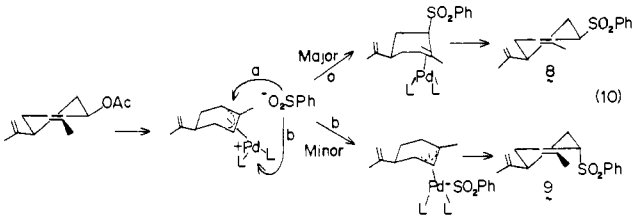
(23) Ozawa, S.; Itoh, A.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1979**, 2909.

(24) Johnson, F. *Chem. Rev.* **1968**, *68*, 375. Also see: Allinger, N. L.; Hirsch, J. A.; Miller, M. A.; Tyminski, I. J. *Ibid.* **1968**, *90*, 5773.

in sulfone esters indicated that exchange α to an ester was faster than α to the sulfone.[25] On the other hand, the fact that **6** and **10** are allylic sulfones might change the relative kinetic acidities. Thus, the base-catalyzed exchange was performed with sodium methoxide in methanol-*O*-*d*, and the results are summarized in Table I. Indeed, entry 1 clearly indicates that exchange α to the sulfone is somewhat more than a factor of 2 faster than exchange α to the ester. Nevertheless, the two protons must have somewhat similar kinetic acidities. The full activating influence of the double bond on increasing the acidity of the sulfone is probably not felt since it is mainly an equatorial proton that must be extracted and such a proton poorly overlaps with the p-orbitals of the olefin. It is also likely that the two conformers of **6** would have different kinetic acidities and that the reactive conformer might actually be **6b** where the proton is better aligned for overlap.

Discussion

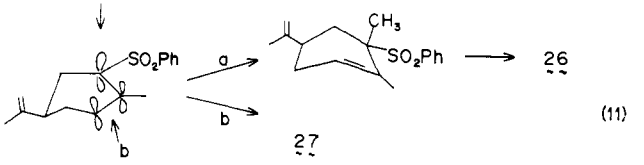
Allylic sulfones are available in stereochemically defined forms by virtually all of the methods used. The preference of a sulfone nucleophile to participate in allylic alkylations catalyzed by palladium with net retention of configuration, albeit with some crossover, is particularly interesting. We have previously established that acetoxy and amine nucleophiles show similar duality, i.e., mainly attack on the π-allylpalladium cationic intermediate directly at carbon (path a, eq 10) but also some leakage by attack



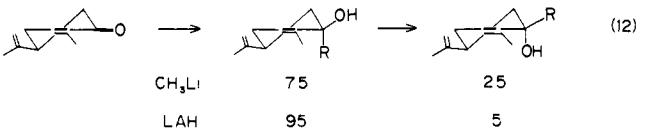
via palladium (path b, eq 10). In the case of acetoxy transfer, excess phosphine, acetate, and chloride ion have been shown to inhibit the latter path and may be a way to minimize crossover in this case as well.[10,26] As can be seen in eq 10, attack directly at carbon forces the cyclohexene to adopt a boat or twist boat conformation as the initial product. The generally preferred direct attack at carbon then may be hampered to some extent due to conformational destabilization of the transition state leading to **8**. Thus, this example may not be reflective of the more general case with respect to the degree of retention of stereochemistry.

This partial ambivalence of reactivity of sulfone agrees with our earlier observations on the classification of nucleophiles in allylic alkylations.[27] Polarizable and soft nucleophiles attack π-allylpalladium complexes directly at carbon. Nonpolarizable and hard nucleophiles attack such complexes through palladium. Heteroatom nucleophiles, which are good ligands for palladium, proceed via both paths with the former preferred. Thus, their electronic characteristics generally place them in the first category, but their propensity to bond to palladium tends to steer them to attack the same face of the allyl fragment that bears palladium. Obviously, the electronic biases dominate but not by much. The ability of a phenylsulfonyl group to bond to Pd(2+) has been demonstrated in Heck-type arylations.[28] Clearly, electronically, a sulfone group belongs to that type of nucleophile that should attack on the π-allyl fragment distal to the metal but its coordinating properties to Pd(2+) compromises its stereochemical course somewhat.

Of prime fundamental importance are the alkylation reactions of sulfonyl stabilized anions which show very reasonable diastereoselectivity (as high as 8:1). Synthetically, the diastereoselectivity is sufficiently high that the pure isomer can be obtained by recrystallization. The unusual stereochemical consequences in the alkylations of **8**, **10**, **28**, and **29** are most striking. In the former case, preferential equatorial alkylation is not what would be expected in the attack on a planar carbanion. To maintain orbital overlap of the allyl conjugation in such a transition state of alkylation, formation of the boat conformation of the initial product as shown in eq 11 results as the initial product leading

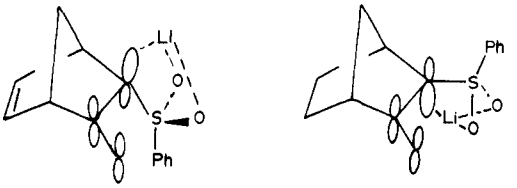


to net equatorial attack. On the other hand, axial attack leading to **27** produces the preferred half-chair conformation directly. While it may be questioned as to the appropriateness of the analogy since the role of electrophile and nucleophile is switched, the steric demands for nucleophilic addition to carvone should parallel those of the alkylation of **8**. Indeed, axial attack dominates as summarized in eq 12.[22,29]



Even more dramatic is the astounding complementarity of stereochemistry of alkylation of **28** and **29**. The isomer which has the greatest steric hindrance for endo attack, i.e., **29**, alkylated predominantly via this path; whereas the isomer which has less steric bias for exo attack, i.e., **28**, proceeds preferentially along this path.

A detailed discussion at this time may be somewhat premature; nevertheless, the notion that such anions are simply charge delocalized allyl anions divorced from the metal is clearly inconsistent with the observations. One possible explanation invokes a partially pyramidalized organometallic species[30-35] as depicted for the anions of **28** and **29** (i.e., **39** and **40**). The endo orientated sulfone in



39 40

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(35) For diastereoselectivity in non-allylic sulfones in six-membered rings see Rothberg, I.; Sundoro, B.; Balanikas, G.; Kirsch, S. *J. Org. Chem.* **1983**, *48*, 4345. Sauer, G. Junghans, K.; Eder, U.; Haffer, G.; Neef, G.; Wiechert, R.; Cleve, G.; Hoyer, G. A. *Liebigs Ann. Chem.* **1982**, *431*. These results also can be rationalized as deriving from the most stable organometallic.

39 may be stabilized by a more favorable σ–π^* interaction between C–S bond and the proximal double bond than would exist in the endo orientated lithium.[32] On the other hand, in the norbornyl series, the unfavorable steric interactions between the sulfone and the 5,6-endo H overwhelms this electronic effect to force the sulfone to be more exo-like. Similar arguments can be advanced to rationalize the stereochemical course of all the reactions.

The preferred axial orientation of the sulfone group in cyclohexenes merits comment. The general notion that a sulfone group is very bulky—one that is supported by its *A* value of 2.5[36]—would indicate that there is an electronic effect that can overwhelm the normal steric effect. A stabilizing π–σ^* interaction would account for this observation. The importance of this electronic effect is best evaluated in the equilibrium between **6a** and **6b** in which the conformer having the phenylsulfonyl group axial, i.e., **6a**, overwhelmingly dominates in spite of the considerably smaller *A* value of a CO_2CH_3 group (1.27) compared to a sulfone. The *E* isomer **9** also shows the phenylsulfonyl group prefers the axial orientation over the isopropenyl group. To some extent, this bias undoubtedly arises from $A_{1,2}$ strain.[37]

The *E*,*Z* equilibria also reinforce this conclusion, i.e., **6** with an axial sulfone is more stable than **10** with an equatorial sulfone. In such an equilibrium, nonbonded interactions which would favor the equatorial sulfone **10** undoubtedly play a role. Indeed, by introducing $A_{1,2}$ strain, we increase the proportion of the axial sulfone isomer at equilibrium. Of course, if such nonbonded interactions work in the opposite direction, the isomer having the sulfone group orthogonal to the π-bond may dominate—as happens in the norbornyl series.

Extending these conclusions to acyclic sulfones which are obviously more conformationally mobile is more difficult. However, the abnormally high field shift of the C(18) methyl group in **14** (δ 0.42) and **25** (δ 0.46) support conformations depicted in **14b** and **25a**—again placing the C–S bond in a conformation for maximum overlap with the bond. While the results reported herein indicate this trend, the generality of these observations must yet be established. Furthermore, the results clearly indicate that several factors operate simultaneously in determining the structure of lithiated allyl sulfones. The importance of lithiated allyl systems and of sulfones in synthesis make the observations reported herein of particular note. Clearly, fundamental questions of the structures of these extremely important intermediates are raised by these results and only partial rationalizations can be profferred at present.

Experimental Section

All reactions were run under a positive pressure of dry nitrogen or argon. Reactions requiring anhydrous conditions were performed in flame-dried glassware which was cooled under nitrogen. Anhydrous solvents were transferred by an oven-dried syringe. Solvents were distilled before use: hexamethylphosphoric triamide (HMPA), dimethyl sulfoxide (Me_2SO), dimethylformamide (DMF), acetonitrile, dichloromethane, pyridine, hexane and pentane from calcium hydride, diethyl ether, tetrahydrofuran (THF), 1,2-dimethoxyethane, 1,4-dioxane from sodium benzophenone ketyl, acetone from barium oxide, and methanol from magnesium. Solvents used in palladium(0)-catalyzed reactions were degassed by bubbling a small stream of argon or nitrogen through the solvent for 20 min. All palladium(0)-catalysts were transferred in a glovebag under a nitrogen atmosphere. After workup all organic layers were dried over anhydrous magnesium sulfate. The term "in vacuo" refers to solvent removal via a Buchi rotoevaporator at water aspirator pressure, followed by evacuation of the flasks at 0.1 torr for several hours. Preparative thin-layer chromatography (TLC) was performed on 20 × 20 or 20 × 40 cm glass plates coated with 1.5 mm of silica gel (Machery-Nagel, MN-Kieselgel, P/UV_{254}, catalog no. 8163880). Analytical TLC was performed on plastic backed plates coated with silica gel (Merck 60-PF254). Column chromatography was performed by using silica gel obtained from W. R. Grace (Grade 62, 60–200 mesh). Preparative high-pressure liquid chromatography (HPLC) was performed on a Waters Prep 500A instrument using either a PrepPak-500 cartridge or a homemade semiprep column (2.5 × 30 cm, μ Poracil, 37–75 μ). Melting points were obtained on a Thomas-Hoover apparatus using open capillary tubes. Melting points are uncorrected.

Proton nuclear magnetic resonance (^{1}H NMR) spectra were determined on a Jeol MH-100 (100 MHz) or a Bruker WH-270 (270 MHz) instrument. Chemical shifts are reported in δ units, parts per million (ppm) downfield from tetramethylsilane. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; br, broad. In spectra where splitting patterns are or may be nonfirst order, the reported apparent coupling constant (J_{app}) refers to peak separations measured directly from such spectra. Coupling constants are reported in hertz (Hz). Infrared spectra (IR) were determined in the indicated solvents in sodium chloride cavity cells on a Perkin-Elmer 267 or a Beckman AccuLab 7. Carbon-13 nuclear magnetic resonance spectra (^{13}C) were determined at 15 MHz on a Jeol FX-60 or at 50 MHz on a Jeol FX-200. Chemical shifts are reported in δ units parts per million downfield from tetramethylsilane. Mass spectra (MS) were obtained on an AEI-902 instrument at an ionizing current of 98 mA and an ionizing voltage of 70 eV unless otherwise noted. Microanalyses were performed by Spang Microanalytical Laboratories, Eagle Harbor, MI, or Galbraith Laboratories, Knoxville, TN. Optical rotations were measured on a Perkin-Elmer 141 or a Perkin-Elmer 241 polarimeter using a microcell (100 mm, 1 mL) in the indicated solvent and concentration (*c*) in grams of solute per 100 mL of solution.

1-(Phenylsulfonyl)-2-butene (1). To a solution of 70% crotyl chloride and 30% 3-chloro-1-butene (Aldrich) (22 mL, 20 g, 0.22 mmol) in 200 mL of methanol was added sodium benzenesulfinate (65.6 g, 0.40 mol). This mixture was refluxed for 16 h and cooled to ambient temperature, and most of the solvent was removed in vacuo. To the remaining slush was added 100 mL of saturated sodium bicarbonate, 200 mL of water, and 150 mL of chloroform. After thorough mixing, the organic layer was separated and the aqueous layer was extracted three additional times with 150-mL portions of chloroform. The combined organic layers were dried and the solvent was removed in vacuo. The resulting oil was distilled from 80–112 °C between 0.15 and 0.40 torr to give 31.6 g (73%) of a mixture containing 97% of an *E*/*Z* mixture of crotyl sulfones and 3% of the corresponding regioisomeric 3-(phenylsulfonyl)-1-butene determined by integration of the signals for the allylic methyl group of **1*E*** and **1*Z*** at δ 1.65 and 1.34 vs. the signal for the regioisomer at δ 1.42. The ratio of **1*E*** to **1*Z*** was 78:22.

For this mixture: IR ($CHCl_3$) 1670, 1590, 1450, 1370, 1350, 1140 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.82 (2 H, m), 7.60 (1 H, m), 7.51 (2 H, m), [5.80 (1 H, m) for **1*Z***], 5.64–5.32 (2 H, m), [5.25 (1 H, d, J = 10.5 Hz), and 5.06 (1 H, d, J = 17.5 Hz) for the minor regioisomer], 3.86 (2 H, d, J = 7.9 Hz) for **1*Z***, 3.74 (1 H, d, J = 7.0 Hz), 1.65 (3 H, d, J = 6.3 Hz), [1.42 (3 H, d, J = 6.5 Hz) for the minor regioisomer], [1.34 (3 H, d, J = 7.0 Hz) for **1*Z***. MS, *m*/*e* (5): 106 (3), 126 (6), 117 (2), 78 (11), 77 (17), 55 (100), 51 (14). Anal. Calcd for $C_{10}H_{12}O_2S$: MW 196.0558; C, 61.20; H, 6.16. Found: MW 196.0558; C, 61.15; H, 6.12.

1-(Phenylsulfonyl)-2-methyl-2-propene (2). This compound was prepared from the allylic chloride (Aldrich) similar to the method described for compound **1**. The following amounts were used: 2-methyl-3-chloro-1-propene (32.3 mL, 30 g, 0.33 mol), sodium benzenesulfinate (82 g, 0.50 mol) in 200 mL of methanol at reflux for 16 h. After removing most of the solvent in vacuo, 300 mL of water was added and the precipitated solid was filtered and washed with three 100-mL portions of water. The crude solid was dried to give 58.2 g (89%) of a white solid, essentially pure as judged by ^{1}H NMR. An analytical sample was recrystallized from 2-propanol to give needles of mp 44–44.5 °C. IR ($CHCl_3$): 1650, 1585, 1450, 1310, 1155, 1130 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.86 (2 H, m), 7.61 (1 H, m), 7.52 (2 H, m), 5.03 (1 H, m), 4.69 (1 H, br s), 3.77 (2 H, s), 1.87 (3 H, dd, J = 1.4, 1.0 Hz). MS, *m*/*e* (%): 196 (1), 141 (5), 132 (29), 131 (15), 126 (12), 117 (14), 82 (12), 78 (20), 77 (53), 56 (12), 55 (100), 53 (13), 51 (30). Anal. Calcd for $C_{10}H_{12}O_2S$: 196.0558. Found: 196.0560.

1-(Phenylsulfonyl)-3-methyl-2-butene (3). This material was prepared according to the procedure described for **1** using the following amounts of materials: prenyl bromide (30 g, 0.20 mol), sodium benzenesulfinate (65.6 g, 0.40 mol), methanol (200 mL). A 63% yield of crude **11** was obtained. This crude material was of sufficient purity to be used in subsequent transformations. An analytical sample was obtained by recrystallization from 2-propanol and displayed a mp 50–51 °C (lit.[38] mp 51–52 °C).

1-(Phenylsulfonyl)-2-phenyl-2-propene (4). 1-Bromo-2-phenyl-2-propene was prepared on a 0.50 mol scale according to the procedure of Reed[39] and used subsequently after workup without purification. To a solution of the preceding bromide in 250 mL of DMF was added sodium

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benzenesulfinate (131 g, 0.80 mol). A slight exotherm was noted. This mixture was heated to 80 °C for 16 h, cooled, and then poured into 800 mL of ice water. This mixture was extracted five times with 200-mL portions of pentane to remove the unreacted α-methylstyrene from the initial bromination. The remaining suspended solid was filtered and washed with 200 mL of water to give 84 g (65%) of a brown solid essentially pure as judged by ^{1}H NMR. An analytical sample was obtained by recrystallization from a hexane/ethyl acetate mixture giving slightly yellow plates of mp 106 °C.

IR ($CHCl_3$): 1630, 1510, 1450, 1320, 1310, 1160, 1145 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.72 (2 H, m), 7.48 (1 H, m), 7.37 (2 H, m), 7.27–7.15 (5 H, m), 5.58 (1 H, s), 5.20 (1 H, s), 4.28 (2 H, s). MS, *m/e* (%): 258 (1), 194 (18), 118 (6), 117 (100), 116 (13), 115 (40), 91 (17), 77 (12), 51 (10). Anal. Calcd for $C_{15}H_{14}O_2S$: 258.0715. Found: 258.0709.

Methyl *trans*-5-(Phenylthio)-3-cyclohexene-1-carboxylate. To a solution of methyl *cis*-5-hydroxy-3-cyclohexene-1-carboxylate (**5**)[40] (332 mg, 2.0 mmol) and triethylamine (303 mg, 3.0 mmol) in 3 mL of methylene chloride at −20 °C was added methanesulfonyl chloride (252 mg, 2.20 mmol). The mixture was stirred for 1 h while maintaining a temperature of between −20 and −10 °C. A second solution of lithium thiophenoxide was prepared by the action of *n*-butyllithium (1.5 mL of a 1.5 M solution in hexane, 2.3 mmol) on thiophenol (236 μL, 2.30 mmol) in 3 mL of THF. The lithium thiophenoxide solution was added to the first solution at −15 °C, and the reaction was then allowed to warm to room temperature. After stirring overnight, the reaction mixture was partitioned between 50 mL of ether and 20 mL of saturated ammonium chloride. The organic layer was separated and dried, and the solvent was removed in vacuo. The crude product was purified by preparative TLC (chloroform) to give two bands. The band at R_f 0.65 consisted of 262 mg (53%) of the pure trans isomer as a colorless oil. The band at R_f 0.37 consisted of 30 mg (6%) of an equimolar mixture of the cis and trans isomers as judged by ^{1}H NMR (the cis isomer at δ 1.72, the trans at δ 1.96).

IR (CCl_4): 1740, 1585, 1480, 1445, 1440 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.40 (2 H, m), 7.24 (3 H, m), 5.82 (2 H, m), 3.92 (1 H, br s), 3.65 (3 H, s), 3.02 (1 H, dddd, J = 11.5, 10.3, 5.5, 3.0 Hz), 2.41–2.12 (3 H, m), 1.96 (1 H, ddd, J = 13.7, 11.7, 4.6 Hz). MS, *m/e* (%): 158 (1), 157 (1), 139 (2), 138 (1), 136 (2), 110 (1), 105 (6), 97 (4), 96 (3), 95 (1), 94 (1), 84 (1), 81 (3), 79 (21), 77 (10), 69 (3), 55 (4), 53 (5), 44 (100). Anal. Calcd for $C_{14}H_{16}O_2S$: MW 248.0871. Found: MW 248.0846.

Methyl (*E*)-5-(Phenylsulfonyl)-3-cyclohexene-1-carboxylate (6). To a solution of the above sulfide (2.52 mmol, 627 mg) in 20 mL of methylene chloride at −78 °C was added MCPBA (5.20 mmol, 1.08 g of material of 85% purity). The cooling bath was removed and the mixture was allowed to warm to room temperature during approximately 20 min. After stirring at room temperature an additional 2 h, the mixture was partitioned between 60 mL of ether and 10 mL of 10% sodium sulfite. The organic layer was further extracted with 10 mL of 10% potassium carbonate. The solvent was removed in vacuo and the crude product was purified by preparative TLC (1/1, hexane ethyl acetate) to give 561 mg (80%) of an oil which solidified upon standing. An analytical sample was recrystallized from 2-propanol to give needles of mp 70.5–71 °C.

IR ($CHCl_3$): 1730, 1655, 1585, 1445, 1380, 1300, 1145 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.90 (2 H, m), 7.70 (1 H, m), 7.58 (2 H, m), 6.14 (1 H, m), 5.72 (1 H, d m, J = 10 Hz), 3.86 (1 H, m, $W_{1/2}$ = 12.3 Hz), 3.67 (3 H, s), 2.94 (1 H, m), 2.42–2.22 (3 H, m), 2.01 (1 H, ddd, J = 14.7, 10.6, 6.6 Hz). ^{13}C NMR (15 MHz, $CDCl_3$): δ 174.5, 137.6, 133.8, 133.7, 129.1, 128.9, 118.0, 60.0, 51.8, 34.8, 26.9, 24.1. MS, *m/e* (%): 248 (18), 142 (29), 140 (48), 139 (100), 138 (15), 125 (14), 111 (24), 107 (47), 93 (3), 91 (4), 81 (34), 80 (54), 79 (99), 78 (45), 77 (27), 67 (13). Anal. Calcd for $C_{14}H_{16}O_4S$: C, 59.98; H, 5.75; S, 11.44; MW 280.0769. Found: C, 59.74; H, 5.78; S, 11.76; MW 280.0774.

(−)-*cis*-Carvyl Acetate (7). To a solution of (−)-*cis*-carveol[41] (1.52 g, 10 mmol) (containing approximately 5–10% of the corresponding trans isomer) in 20 mL of methylene chloride was added acetic anhydride (1.53 g, 15 mmol) and triethylamine (2.02 g, 20 mmol). With addition of 4-(dimethylamino)pyridine (20 mg, 0.16 mmol) the reaction mixture was warmed slightly. After about 15 min the reaction was complete as judged by TLC. The reaction mixture was partitioned between 100 mL of hexane and 50 mL of 10% hydrochloric acid. The organic layer was further extracted with 50 mL of 10% sodium hydroxide, and the solvent was removed in vacuo to give a 2.01 g (96%) of a light yellow oil after filtration through a short plug of silica gel (hexane).

IR ($CHCl_3$): 1730, 1650, 1455, 1435, 1370 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$): δ 5.59 (1 H, br s), 5.43 (1 H, br s, $W_{1/2}$ = 20 Hz), 4.72 (2 H, s), 2.29 (1 H, m), 2.25–1.65 (3 H, m), 2.08 (3 H, s), 1.76 (3 H, s), 1.64 (3 H, m), 1.49 (1 H, q d, J = 12.8, 10.7 Hz). MS *m/e* (%): 194 (1), 152 (46), 134 (50), 119 (73), 109 (44), 105 (14), 93 (23), 91 (36), 84 (75), 82 (13), 79 (13), 77 (14), 55 (14), 43 (100). Anal. Calcd for $C_{12}H_{18}O_2$: MW 194.1307; C, 74.19; H, 9.34. Found: MW 194.1307; C, 73.94; H, 9.24.

(*Z*)- and (*E*)-[(2-Methyl-5-(1-methylethenyl)-2-cyclohexen-1-yl)-sulfonyl]benzene (8a and 9a). To a solution of the *cis*-allylic acetate **7** (containing 8% of the trans isomer) (175 mg, 0.90 mmol) in 4 mL of DME was added sodium benzenesulfinate (1.00 g, 6.09 mmol) and bis-[1,2-bis(diphenylphosphino)ethane]palladium(0) (40 mg, 0.044 mmol). This mixture was refluxed for 16 h after which time the reaction was judged to be incomplete so an additional 75 mg (0.083 mmol) of the palladium catalyst was added and the mixture was refluxed for an additional 24 h. The mixture was then partitioned between 75 mL of ether and 25 mL of saturated sodium bicarbonate. The organic layer was then extracted with 25 mL of water, separated, and dried, and the solvent was removed in vacuo. The crude product was then purified by preparative TLC using a hexane/ethyl acetate eluent (4/1) to give 178 mg (71%) of a 72:27 mixture of **8a** and **9a** as judged by ^{1}H NMR integration of the signals at δ 3.96 and 3.74, respectively.

For the mixture: IR ($CHCl_3$): 1650, 1590, 1450, 1300, 1140 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.89 (2 H, m), 7.63 (1 H, m), 7.55 (2 H, m), [5.84 (1 H, ?) minor isomer], 5.80 (1 H, br d, J = 6.5 Hz), 4.68 (1 H, m), 4.58 (1 H, m), 3.96 (1 H, br s, $W_{1/2}$ = 21 Hz), [3.74 (1 H, br d, J = 5 Hz, $W_{1/2}$ = 11 Hz) minor isomer], [2.46 (1 H, br m) minor isomer], 2.20–1.50 (4 H, m), 2.05 (3 H, s), [1.99 (3 H, s) minor isomer], [1.62 (3 H, s) minor isomer], 1.60 (3 H, s). MS *m/e* (%): 136 (5), 135 (61), 314 (14), 107 (55), 93 (100), 91 (18), 79 (17), 77 (25), 69 (3), 55 (19). Anal. Calcd for $C_{16}H_{20}O_2S$: C, 69.53; H, 7.29; S, 11.60. Found: C, 69.38; H, 7.22; S, 11.52.

(*Z*)- and (*E*)-4-Bromo[(2-methyl-5-(1-methylethenyl)-2-cyclohexen-1-yl)sulfonyl]benzene (8b and 9b). To a solution of the *cis*-allylic acetate **7** (containing 3% of the trans isomer) (2.90 g, 14.9 mmol) in 150 mL of methanol was added sodium *p*-bromobenzenesulfinate (16.51 g, 68 mmol) and tetrakis(triphenylphosphine)palladium (245 mg, 0.21 mmol). The mixture was refluxed for 16 h and cooled to ambient temperature, and most of the solvent was removed in vacuo. The remaining material was partitioned between 200 mL of ether and 200 mL of water. The organic layer was then washed with 200 mL of 10% sodium hydroxide, separated, and dried, and the solvent was removed in vacuo. The crude material was then partially purified by column chromatography on 75-cm^3 silica gel eluting first with hexane, then with 5% ethyl acetate/hexane. From the hexane fraction was isolated 1.16 g (40%) of the starting material **7**. The ethyl acetate/hexane fraction contained 2.58 g of a mixture of **8b** and **9b** in a ratio of 63/37 based on ^{1}H NMR integration of the signals at δ 3.94 and 3.71, respectively. This mixture was then further purified by HPLC (4% ethyl acetate/hexane). Partial separation of the *Z* and *E* isomers was achieved with the *E* isomer being eluted first. The first fraction containing product had an *E* to *Z* ratio of 4:1, while the last product containing fraction had an *E* to *Z* ratio of 1:3. Pure **8b** was obtained by crystallization of one of the later LC fractions from 0.5% ethyl acetate in hexane. This material had a melting point of 91–92 °C.

For **8b**: IR ($CHCl_3$): 1650, 1570, 1475, 1455, 1440, 1390, 1360, 1140 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.71 (4 H, m), 5.88 (1 H, m), 4.71 (1 H, quintet, J = 1.5 Hz), 4.61 (1 H, m), 3.94 (1 H, m), 2.10–1.50 (3 H, m), 2.05 (3 H, s), 1.64 (3 H, s), [1.61 (1 H, qd, J = 12.9, 10.7 Hz) ? partially obscured by other signals. MS, *m/e* (%): 221 (1), 219 (1), 157 (20), 155 (20), 135 (65), 134 (13), 119 (24), 108 (15), 107 (94), 105 (30), 94 (23), 93 (100), 92 (18), 91 (71), 81 (10), 79 (62), 78 (13), 77 (64), 76 (23), 75 (25), 55 (79), 53 (30). Anal. Calcd for $C_{16}H_{19}BrO_2S$: C, 54.09; H, 5.39; Br, 22.49; S, 9.03. Found: C, 54.06; H, 5.42; Br, 22.66; S, 9.16.

Methyl (*Z*)-5-(Phenylsulfonyl)-3-cyclohexene-1-carboxylate (10). To a solution of methyl *cis*-3-cyclohexene-5-ol-1-carboxylate[40] (10 mmol, 1.56 g) in 15 mL of THF at −78 °C was added a solution of *n*-butyllithium in hexane. After 5 min a solution of benzenesulfenyl chloride[42] (10 mmol, 25 mL of 0.4 M solution) in methylene chloride was added. The red orange color of the benzenesulfenyl chloride seemed to be instantly discharged. An additional 10 mL of the benzenesulfenyl chloride was added until the persistence of a faint orange color was observed. The

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reaction was allowed to warm to room temperature during approximately 30 min. The mixture was partitioned between 100 mL of ether and 50 mL of 10% sodium hydroxide. The organic layer was then washed with 50 mL of saturated ammonium chloride. The solvent was removed in vacuo, and the crude orange oil was purified by column chromatography on silica gel (hexane/ethyl acetate gradient) to give 1.52 g (56%) of the product contaminated with approximately 10% of an impurity whose structure is tentatively assigned to be *Z*-1-phenylsulfinyl-5-(1-hydroxy-1-butylpentyl)cyclohex-2-ene resulting from *n*-butyllithium attack on the ester. This mixture was oxidized subsequently without further purification.

IR (CCl_4): 1740, 1060 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 7.68 (2 H, m), 7.52 (2 H, m), 6.08 (1 H, m), 5.78 (1 H, m), 3.67 (3 H, s), 3.52 (1 H, m), 2.53 (1 H, m), 2.40–1.90 (3 H, m), 1.76 (1 H, qd, J = 12.5, 11.0 Hz), with signals for the impurity at 1.61–1.20 (m) and 0.90 (m).

To a solution of the above sulfoxide (111 mg, 0.42 mmol) in 4 mL of methylene chloride at −78 °C was added solid 85% *m*-chloroperbenzoic acid (112 mg, 0.55 mmol). The reaction was allowed to warm to room temperature during 2 h and the mixture partitioned between 50 mL of ether and 25 mL of 10% sodium hydroxide. The organic layer was separated and dried, and the solvent was removed in vacuo. The crude oil was purified by preparative TLC (2/1, ethyl acetate/hexane) to give 63 mg (54%) of a solid. An analytical sample was recrystallized from a hexane/ethyl acetate mixture to give a solid melting at 90 °C.

IR ($CHCl_3$): 1735, 1650, 1590, 1450, 1440, 1380, 1300, 1150 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 7.88 (2 H, m), 7.60 (1 H, m), 7.57 (2 H, m), 6.03 (1 H, m), 5.89 (1 H, d m, J = 10 Hz), 3.86 (1 H, m, $W_{1/2}$ = 24 Hz), 3.68 (3 H, s), 2.54 (1 H, m), 2.32–2.25 (2 H, m), 2.09 (1 H, m), 1.70 (1 H, t d, J = 13.0, 11.8 Hz). ^{13}C NMR (15 MHz, $CDCl_3$): δ 173.8, 136.4, 133.6, 132.3, 128.8, 118.7, 62.4, 51.7, 37.9, 27.1, 25.3. MS (30 eV), *m/e* (%): 249 (1), 205 (2), 143 (4), 140 (6), 139 (100), 138 (1), 125 (10), 111 (3), 107 (4), 105 (3), 80 (8), 79 (84), 77 (7). Anal. Calcd for $C_{14}H_{16}O_4S$: C, 59.98; H, 5.75; S, 11.44; MW 280.0769. Found: C, 60.13; H, 6.00; S, 11.29; MW 280.0766.

20-(Phenylsulfonyl)-6β-methoxy-3α,5-cyclo-21-nor-5α-pregn-16-ene (16). To a solution of alcohol **11**[13] (352 mg, 1.11 mmol) in 15 mL of THF at −78 °C was added 1.3 mL (1.11 mmol) of a 1.4 M solution of *n*-butyllithium in hexane. After stirring for 30 min at this temperature, neat benzenesulfenyl chloride[42] was added dropwise until the red color persisted (after 200 μL). The solution was allowed to warm to room temperature over 3 h, and the mixture was partitioned between 50 mL of ether and 50 mL of saturated sodium bicarbonate. The organic layer was separated and dried, and the solvent was removed in vacuo. The crude product was purified by preparative TLC (2/1, hexane/ethyl acetate) to give 325 mg (69%) of a mixture of diastereomeric sulfoxides. A ^1H NMR spectrum of this mixture was recorded but it was not characterized further.

^1H NMR (270 MHz, $CDCl_3$): δ 7.63 (2 H, m), 7.50 (3 H, m), 5.64 (1 H, br s), 3.35 (3 H, s), 1.06 (3 H, s), 0.86 (3 H, s), with a signal for the minor isomer at δ 5.47 (br s).

The preceding mixture of sulfoxides (325 mg, 0.76 mmol) was dissolved in 15 mL of chloroform. The solution was cooled to −30 °C and to it was added a solution of 85% *m*-chloroperbenzoic acid (153 mg, 0.75 mmol) in 1 mL of the same solvent. The cooling bath was removed, and the mixture was allowed to warm to room temperature during 1 h. The mixture was then partitioned between 75 mL of ether and 25 mL of 10% sodium hydroxide. The organic layer was separated and dried, and the solvent was removed in vacuo. The crude product was purified by preparative TLC (2:1, hexane/ethyl acetate) to give 255 mg (76%) of the product **12** as a foam.

IR ($CHCl_3$): 1625, 1590, 1450, 1375, 1320, 1305, 1150 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): 7.88 (2 H, m), 7.62 (1 H, m), 7.52 (2 H, m), 5.72 (1 H, br s), 3.85 (1 H, A of AB, J = 14.7 Hz), 3.76 (1 H, B of AB, J = 14.8 Hz), 3.35 (3 H, s), 2.13 (1 H, ddd, J = 15.0, 6.3, 2.6 Hz), 1.03 (3 H, s), 0.72 (3 H, s). MS *m/e* (%): 440 (7), 425 (16), 408 (12), 385 (36), 368 (18), 267 (100), 266 (12), 253 (12), 251 (12), 185 (10), 173 (10), 161 (10), 159 (23), 147 (10), 145 (20), 107 (40), 105 (30), 95 (20). Anal. Calcd for $C_{27}H_{36}O_3S$: 440.2385. Found: 440.2379.

(20*S*)-20-(Phenylsulfonyl)-6β-methoxy-3α,5-cyclo-5-pregn-16-ene (14). The 16α-alcohol **13**[13] (2.01 g, 6.09 mmol) was dissolved in 25 mL of benzene and most of the benzene was distilled in order to remove any water. The remaining solvent was removed in vacuo (not all solvent could be removed due to excess foaming). To the dried alcohol, 25 mL of THF and then a solution of 1.6 M *n*-butyllithium in hexane (4.1 mL, 6.5 mmol) was added. After stirring at −78 °C for 15 min, neat benzenesulfenyl chloride[45] (765 μL, 1.14 g, 7.91 mmol) was added dropwise until the red color of the sulfenyl chloride persisted. The reaction was allowed to proceed as above for 1 h and then worked up as outlined using sodium hydroxide as the base wash. The crude product was purified by HPLC (25% ethyl acetate/hexane) to give 2.15 g (80%) of a 64/36 mixture of sulfoxides (epimeric at sulfur). A ^1H NMR spectrum of this mixture was recorded, but it was not characterized further. For the major sulfoxide isomer: ^1H NMR (270 MHz, $CDCl_3$) δ 5.82 (1 H, br s, CH-16), 3.20 (1 H, q, J = 6.9 Hz, CH-21), 1.33 (3 H, d, J = 7.0 Hz, CH_3-21), 1.03 (3 H, s, CH_3-19), 0.60 (3 H, s, CH_3-18). For the minor sulfoxide isomer: ^1H NMR (270 MHz, $CDCl_3$) δ 5.48 (1 H, br s, CH-16), 3.57 (1 H, q, J = 7 Hz, CH-21), 1.14 (3 H, d, J = 7.0 Hz, CH_3-21), 1.04 (3 H, s, CH_3-19), 0.90 (3 H, s, CH_3-18). (The preceding data was obtained from the mixture of sulfoxides. No attempt was made to separate the compounds.)

The preceding mixture of sulfoxides (2.15 g, 4.90 mmol) was oxidized with MCPBA (995 mg of 85% pure, 4.90 mmol) in 150 mL of chloroform as above. After 15 min at room temperature there still appeared to be some remaining starting material, so an additional 60 mg (0.30 mmol) portion of the solid peracid was added. After an additional 30 min, the reaction mixture was partitioned between 100 mL of chloroform and 25 mL of water and worked up as above. The crude product was purified by preparative HPLC (10% ethyl acetate/hexane) to give 1.60 g (72%) of the sulfone **14** as a foam. An analytical sample was obtained by recrystallization from hexane to give small "rocklets" of mp 125–127 °C.

IR ($CHCl_3$): 1450, 1370, 1150 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 7.80 (2 H, AA′ of AA′XYY′, J_{app} = 8 Hz), 7.61 (1 H, X of AA′XYY′, J_{app} = 7.3, 2.5 Hz), 7.51 (2 H, YY′ of AA′XYY′, J_{app} = 7.8, 1.4 Hz), 6.11 (1 H, dd, J = 2.5, 1.0 Hz), 3.59 (1 H, q, J = 7.0 Hz), 3.33 (3 H, s), 2.78 (1 H, t, J = 2.7 Hz), 2.12 (1 H, ddd, J = 15.0, 6.2, 3.2 Hz, CH-15), 1.51 (3 H, d, J = 7.0 Hz), 1.01 (3 H, s), 0.65 (1 H, t, J = 4.3 Hz), 0.46 (1 H, dd, J = 7.6, 5.1 Hz), 0.42 (3 H, s). MS (20 eV), *m/e* (%): 439 (0.1), 422 (1), 314 (5), 313 (33), 282 (36), 281 (100), 173 (5), 159 (5), 135 (5), 121 (21), 110 (9). Anal. Calcd for $C_{28}H_{38}O_3S$: MW 454.2542; C, 73.96; H, 8.42; S, 7.05. Found: MW 454.2540; C, 74.19; H, 8.29; S, 7.02.

(20*R*)-20-(Phenylsulfonyl)-6β-methoxy-3α,5-cyclo-5α-pregn-16-ene (17). The 16α-alcohol **15**[13] (1.06 g, 3.21 mmol), dried as above, was reacted with *n*-butyllithium (2.40 mL of 1.6 M solution in hexane, 3.85 mmol) and benzenesulfenyl chloride[42] (400 μL, 600 mg, 4.1 mmol) as above. After workup as described above, the crude product was separated by HPLC (25% ethyl acetate/hexane) to give 147 mg (14%) of recovered starting material, 291 mg (28%) of enone, and 361 mg (26%) of a mixture of sulfoxides in a 62/38 ratio. A ^1H NMR spectrum of this mixture was recorded, but the material was not characterized further.

For the major sulfoxide isomer: ^1H NMR (270 MHz, $CDCl_3$) δ 5.80 (1 H, br s, CH-16), 3.35 (3 H, s, OCH_3), 3.19 (1 H, q, J = 7 Hz, CH-21), 1.29 (3 H, d, J = 7.0 Hz, CH_3-21), 1.04 (3 H, s, CH_3-19), 0.83 (s, CH_3-18).

For the minor sulfoxide isomer: ^1H NMR (270 MHz, $CDCl_3$) δ 5.24 (1 H, br s, CH-16), 3.63 (1 H, q, J = 7 Hz), 3.36 (3 H, s, OCH_3), 1.16 (3 H, d, J = 7.0 Hz, CH_3-21), 1.07 (3 H, s, CH_3-19), 0.85 (3 H, s, CH_3-18). (The preceding data was obtained from the mixture of sulfoxides. No attempt was made to separate these compounds.)

The preceding mixture of sulfoxides (361 mg, 0.82 mmol) was oxidized in 10 mL of chloroform at room temperature with 85% MCPBA (0.82 mmol, 167 mg) in 2 mL of the same solvent as above. After workup, the crude product was separated by preparative TLC (33% ethyl acetate/hexane) to give 188 mg (50%) of the sulfone which solidified on standing to give a solid of mp 178–180 °C. An analytical sample was obtained by recrystallization from hexane/ethyl acetate mixture to give needles of mp 196–197 °C.

IR ($CHCl_3$): 1590, 1450, 1375, 1300 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 7.84 (2 H, AA′ of AA′XYY′, J_{app} = 8 Hz), 7.64 (1 H, X of AA′XYY′, J = 7.8, 2.3 Hz), 7.54 (2 H, YY′ of AA′XYY′, J_{app} = 7.8, 1.5 Hz), 5.83 (1 H, m), 3.65 (1 H, q, J = 7.0 Hz), 3.34 (3 H, s), 2.80 (1 H, t, J = 2.6 Hz), 2.19 (1 H, ddd, J = 15, 6, 3 Hz, H-15α), 1.48 (3 H, d, J = 7.4 Hz), 1.03 (3 H, s), 0.77 (3 H, s), 0.66 (1 H, t, J = 4.3 Hz), 0.46 (1 H, dd, J = 7.8, 5.0 Hz). MS (30 eV), *m/e* (%): 374 (5), 359 (7), 347 (8), 346 (49), 342 (7), 331 (60), 330 (36), 328 (11), 319 (12), 315 (33), 314 (61), 313 (24), 213 (30), 297 (20), 291 (100), 281 (36), 275 (22), 257 (25), 214 (71), 199 (20), 173 (16), 159 (35), 145 (27), 137 (21), 135 (26), 133 (23), 121 (37), 119 (10), 109 (31), 107 (39), 105 (31), 95 (31), 93 (27). Anal. Calcd for $C_{28}H_{38}O_3S$: MW 454.2542; C, 73.96; H, 8.42; S, 7.05. Found: MW 454.2563; C, 74.05; H, 8.67, S, 6.99.

3-(Phenylsulfonyl)-2-phenyl-1-heptene (19). To a solution of sulfone **4** (20 mmol, 5.17 g), in 20 mL THF at −78 °C was added *n*-butyllithium (15.3 mL of 1.5 M solution in hexane, 23 mmol). The cooling bath was removed and the mixture was allowed to warm to room temperature. This solution was added to neat *n*-butyl iodide (60 mmol, 11.0 g) at such a rate that the THF gently refluxed. After the addition was complete,

the mixture was stirred for 5 min and then partitioned between 100 mL of ether and 50 mL of saturated ammonium chloride. The solvent and excess *n*-butyl iodide were removed in vacuo to yield 5.91 g (94%) of the product as a light yellow oil contaminated with a small amount of dialkylated product. The product was further purified by recrystallization from hexane to give colorless plates of mp 60–60.5 °C.

IR ($CHCl_3$): 1615, 1495, 1445, 1310, 1200 cm^{-1}. ^1H NMR (100 MHz, $CDCl_3$): δ 7.88 (2 H, m), 7.55 (3 H, m), 7.24 (5 H, br s), 5.65 (1 H, s), 5.55 (1 H, s), 4.16 (1 H, dd, J = 11, 4 Hz), 2.45–1.00 (6 H, m), 0.84 (3 H, m). MS (20 eV), m/e (%): 213 (21), 185 (9), 173 (28), 172 (100), 143 (26), 129 (19), 117 (10), 105 (25), 91 (32). Anal. Calcd for $C_{19}H_{22}O_2S$: MW 314.1340; C, 72.57; H, 7.05; S, 10.20. Found: MW 314.1325; C, 72.49; H, 7.02; S, 10.25.

2-Methyl-3-(phenylsulfonyl)-1-heptene (20). This material was prepared in a manner similar to that described for **19** using the following amounts of reagents and solvents: sulfone **2** (1.96 g, 10.0 mmol), 1.5 M *n*-butyllithium (8 mL, 12 mmol), *n*-butyl iodide (4 mL, 6.48 g, 35 mmol), and THF (25 mL). The crude product was purified by HPLC (5% ethyl acetate/hexane) to give 2.23 g (88%) of material that was contaminated with 15% dialkylated material as judged by ^1H NMR integration of the signals between δ 4.50–5.00 (mono- and dialkylated product) vs. the signal at δ 3.50 (monoalkylated product only). Pure **15** could be isolated by recrystallization from hexane to give a solid of mp 50–53 °C.

IR ($CHCl_3$): 3080, 3040, 2990, 2960, 2900, 1650, 1590, 1450, 1305, 1150, 1090, 915 cm^{-1}. ^1H NMR (100 MHz, $CDCl_3$): δ 7.92 (2 H, m), 7.60 (3 H, m), 5.00 (1 H, s), 4.68 (1 H, s), 3.50 (1 H, dd, J = 11, 4 Hz), 2.30–1.00 (6 H, m), 1.80 (3 H, s), 0.85 (3 H, m). MS (30 eV), m/e (%): 143 (7), 131 (1), 125 (3), 111 (71), 110 (84), 95 (14), 81 (11), 70 (12), 69 (100), 68 (19), 55 (90). Anal. Calcd for $C_{14}H_{20}O_2S$: 252.1176. Found: 252.1180.

2-Methyl-4-(phenylsulfonyl)-(*E*)-2-octene (21). To a solution of sulfone **3** (2.10 g, 10 mmol), in 8 mL of THF at −78 °C was added a solution of 1.5 M *n*-butyllithium (6.7 mL, 10 mmol) in hexane. A red color was immediately produced. This mixture was allowed to warm to room temperature. At room temperature a large amount of solid was present. Upon addition of 1 mL of HMPA, the solution color became more intensely red and the solid dissolved. This solution was added via cannula to a mixture of 4 mL of HMPA and **4** mL of *n*-butyl iodide causing a slight exotherm. This mixture was stirred for 10 min and partitioned between 100 mL of hexane and 100 mL of water. The organic layer was extracted once more with 100 mL of water, separated, and dried, and the solvent was removed in vacuo. The crude product was purified by column chromatography to give 1.94 g (73%) of an oil that solidified on standing (mp 55–60 °C). An analytical sample was obtained by recrystallization from methanol to give needles of mp 59–60 °C.

IR ($CHCl_3$): 1670, 1585, 1445, 1375, 1290, 1150 cm^{-1}. ^1H NMR (100 MHz, $CDCl_3$): δ 7.78 (2 H, m), 7.50 (3 H, m), 4.90 (1 H, br d, J = 11 Hz), 3.72 (1 H, td, J = 10, 4 Hz), 2.30 (1 H, m), 1.91–1.10 (5 H, m), 1.68 (3 H, s), 1.20 (3 H, s), 0.85 (3 H, m). MS, m/e (%): 143 (2), 95 (6), 83 (21), 82 (7), 81 (9), 78 (9), 77 (25), 70 (10), 69 (100), 67 (20), 55 (37), 53 (10), 43 (12), 41 (81). Anal. Calcd for $C_{15}H_{22}O_2S$: MW 266.1340; C, 67.62; H, 8.33; S, 12.04. Found: MW 266.1341; C, 67.67; H, 8.34; S, 12.18.

2-Phenyl-3-(phenylsulfonyl)-1-hepten-6-one (22). To a solution of sulfone **4** (516 mg, 2.00 mmol) in 4 mL of THF at −78 °C was added a solution of 1.5 M *n*-butyllithium (1.4 mL, 2.1 mmol) in hexane. An intense red color developed instantly. This mixture was allowed to warm to 0 °C over 2 h, then recooled to −78 °C. Neat methyl vinyl ketone (190 μL, 161 mg, 2.3 mmol) was added. The mixture was stirred at −78 °C for 2 h and then quenched by the addition of 1 mL of methanol. The mixture was then partitioned between 150 mL of ether and 50 mL of water. The organic layer was then extracted with 50 mL saturated ammonium chloride, separated, and dried, and the solvent was removed in vacuo. The crude product was purified by preparative TLC (1/1, hexane/ethyl acetate) to give 412 mg (63%) of ketone **22** as an oil.

IR ($CHCl_3$): 1720, 1455, 1310, 1150 cm^{-1}. ^1H NMR (100 MHz, $CDCl_3$): δ 7.72 (2 H, m), 7.38 (3 H, m), 7.05 (5 H, br s), 5.46 (1 H, s), 5.32 (1 H, s), 4.18 (1 H, m), 2.60–1.90 (4 H, m), 1.84 (3 H, s). MS, m/e (%): 271 (3), 194 (7), 188 (39), 187 (72), 186 (7), 145 (23), 143 (19), 130 (36), 129 (82), 128 (40), 117 (45), 115 (21), 105 (24), 91 (19), 43 (100). Anal. Calcd for $C_{19}H_{20}O_3S$: 328.1133. Found: 328.1128.

2-Methyl-3-(phenylsulfonyl)-1-hepten-6-one (23). To a solution of sulfone **2** (3.93 g, 20 mmol) in 50 mL of THF at −78 °C was added 15.3 mL (23 mmol) of a 1.5 M solution of *n*-butyllithium in hexane. The yellow heterogeneous solution was allowed to warm to 0 °C over 1 h and then recooled to −78 °C. To this solution 2.03 mL (1.5 g, 25 mmol) of methyl vinyl ketone was added dropwise. The mixture was allowed to warm to −5 °C during 2 h and then recooled to −78 °C and quenched with 2 mL of acetic acid. The mixture was then partitioned between 50 mL of water and 200 mL of ether. The organic layer was then extracted with 50 mL of saturated sodium bicarbonate, separated, and dried, and the solvent was removed in vacuo. The crude product was separated on a column of 50 g of silica gel using an ethyl acetate/hexane gradient to give 3.22 g (62%) of the product as an oil which solidified on standing. An analytical sample was obtained by recrystallization from 2-propanol to give a solid of mp 66–67 °C.

IR ($CHCl_3$): 1715, 1645, 1590, 1450, 1370, 1305, 1155 cm^{-1}. ^1H NMR (100 MHz, $CDCl_3$): δ 7.90 (2 H, m), 7.63 (3 H, m), 5.08 (1 H, m), 4.80 (1 H, br s), 3.75 (1 H, dd, J = 10, 4 Hz), 2.70–1.95 (4 H, m), 3.08 (3 H, s), 1.76 (3 H, s). MS, m/e (%): 248 (1), 209 (10), 196 (18), 195 (2), 179 (4), 161 (7), 149 (1), 143 (5), 141 (3), 135 (1), 131 (5), 130 (18), 129 (12), 126 (20), 125 (77), 110 (16), 109 (12), 107 (30), 91 (15), 81 (26), 79 (12), 78 (27), 77 (40), 71 (32), 91 (15), 81 (26), 79 (12), 78 (27), 77 (40), 71 (32), 67 (32), 55 (45), 43 (100). Anal. Calcd for $C_{14}H_{18}O_3S$: 266.0977. Found: 266.0976.

2-Methyl-4-(phenylsulfonyl)-2-octen-7-one (24). This material was prepared in a manner similar to that described for the preparation of **23**. The reaction was allowed to proceed for 40 min at −78 °C before quenching with methanol. The following amounts of reagents and solvents were used: sulfone **3** (840 mg, 4.00 mmol), 1.5 M *n*-butyllithium (2.7 mL, 4.10 mmol), methyl vinyl ketone (332 μL, 287 mg, 4.10 mmol). After purification by preparative TLC (2/1, hexane/ethyl acetate) 280 mg (33%) of the starting sulfone **3** was isolated, along with 329 mg (29%, 44% based on recovered **3**) of the ketone **24**.

IR ($CHCl_3$): 1720, 1450, 1360, 1200, 1145 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 7.81 (2 H, m), 7.62 (1 H, C of AA'BB'C, J_{app} = 7.5, 2.5 Hz), 7.52 (2 H, m), 4.90 (1 H, d m, J = 10.4 Hz), 3.87 (3 H, s), 1.88 (1 H, m), 1.67 (3 H, d, J = 1.3 Hz), 1.19 (3 H, d, J = 1.3 Hz). MS, m/e (%): 210 (1), 143 (1), 140 (25), 139 (83), 121 (50), 95 (49), 93 (10), 86 (16), 81 (57), 67 (20), 59 (41), 43 (100). Anal. Calcd for $C_{15}H_{20}O_3S$: 280.1133. Found: 280.1134.

Methyl (20*R*)-(Phenylsulfonyl)-6β-methoxy-3α,5-cyclo-21-nor-5α-chol-16-enoate (25). To a solution of sulfone **12** (100 mg, 0.23 mmol) and methyl acrylate (20 μL, 19.5 mg, 0.23 mmol) in 5 mL of THF was added 500 μL of a 2.0 M solution of potassium *tert*-butoxide in 2-methyl-2-propanol (1 mmol). The resulting yellow solution was stirred at this temperature for 2 h and quenched by the addition of 1 mL of acetic acid. The resulting mixture was then partitioned between 50 mL of ether and 20 mL of saturated sodium bicarbonate. The organic layer was separated and dried, and the solvent was removed in vacuo. The crude product was purified by preparative TLC (1/2, ethyl acetate/hexane) to give 93 mg (77%) of the product along with some unidentified impurities. The product appears to be an approximately 4/1 mixture of diastereomers (with the major isomer being assigned the 20*R* configuration) as determined by ^1H NMR integration [for the major isomer δ 6.03 (m, CH-16) and for the minor isomer δ 5.81 (m, CH-16)].

IR ($CHCl_3$): 1735, 1500, 1480, 1305, 1145 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 7.83 (2 H, m), 7.38 (1 H, m), 7.22 (2 H, m), 6.03 (1 H, br s), 3.65 (3 H, s), 3.33 (3 H, s), 1.01 (3 H, s), 0.46 (3 H, s) with signals for the minor isomer at 3.62, 3.35, 1.04 and 0.77. MS, m/e (%): 457 (15), 425 (27), 385 (29), 354 (14), 353 (76), 159 (11), 121 (12), 110 (11), 78 (25). Anal. Calcd for $C_{31}H_{42}O_5S$: 526.2753. Found: 526.2753.

(1*R,5*S**)-[(1,2-Dimethyl-5-(1-methylethenyl)-2-cyclohexen-1-yl)-sulfonyl]benzene (26a).** To an 82/18, *Z*/*E* mixture of sulfones **8a** and **9a** (330 mg, 1.19 mmol) in 20 mL of THF at −78 °C was added dropwise a 1.6 M solution of *n*-butyllithium (895 μL, 1.40 mmol). This mixture was stirred at this temperature for 30 min after which time neat methyl iodide (1 mL, 2.14 g, 15 mmol) was added. After warming to room temperature during 1 h, the mixture was partitioned between 50 mL of ether and 25 mL of 10% hydrochloric acid. The organic layer was separated and dried, and the solvent was removed in vacuo to give a crude product that was purified by preparative TLC (3/1, hexane/ethyl acetate) to give 304 mg (88%) of a mixture of two sulfones **26a** and **27a** in an 88/12 ratio as judged by ^1H NMR integration (for **26** a signal at δ 5.90 and for **27a** a signal at δ 5.73). The major isomer **26a** was obtained by recrystallization from hexane to give needles of mp 78.5–79 °C.

IR ($CHCl_3$): 1650, 1590, 1450, 1310, 1300, 1150 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 7.85 (2 H, m), 7.62 (1 H, m), 7.54 (2 H, m), 5.90 (1 H, m), 4.68 (1 H, m), 4.61 (1 H, s), 2.57 (1 H, m), 2.20–1.75 (3 H, m), 2.02 (3 H, m), 1.64 (3 H, s), 1.52 (3 H, s), 1.37 (1 H, dd, J = 14.7, 13.6 Hz). ^{13}C NMR ($CDCl_3$), 15 MHz): δ 148.1, 133.4, 132.0, 130.0, 129.0, 128.6, 109.3, 67.6, 38.1, 35.6, 30.7, 22.8, 20.4, 20.3. MS (35 eV), m/e (%): 262 (8), 171 (24), 170 (8), 149 (48), 148 (8), 107 (96), 106 (16), 105 (24), 93 (24), 91 (40), 79 (16), 77 (24), 69 (16), 44 (100). Anal. Calcd for $C_{17}H_{22}O_2S$: MW 290.1340; C, 70.30; H, 7.64; S, 11.04. Found: MW 290.1329; C, 70.35; H, 7.66; S, 10.95.

(1*R,5*S**)-4-Bromo[(1,2-dimethyl-5-(1-methylethenyl)-2-cyclohexen-1-yl)sulfonyl]benzene (26b).** To a 63/37 cis/trans mixture of

sulfones **8b** and **9b** (878 mg, 2.47 mmol) in 4 mL of THF at −78 °C was added dropwise a solution of lithium diisopropylamide [prepared from diisopropylamine (494 μL, 357 mg, 3.50 mmol) and *n*-butyllithium (1.9 mL of a 1.55 M solution, 2.96 mmol) in 4 mL of THF]. An immediate intense red color was produced. This solution was allowed to warm to room temperature during 20 min, then recooled to −78 °C. To this solution was added neat methyl iodide (2 mL, 4.28 g, 30 mmol) whereupon most of the color was discharged. After reaction and workup as for the above case, the crude product was first purified by filtration through a short silica gel plug (5% ethyl acetate/hexane) to give the products in a 77/23 ratio as judged by ^{1}H NMR [signal for the major 1*R**,5*S** isomer **26b** of δ 5.92 and signal for the minor isomer **27b** at δ 5.76]. Subsequent purification was performed by HPLC (2% ethyl acetate/hexane) to give two initial fractions containing 43 mg of the pure major 1*R**,5*S** isomer **26b** and 590 mg of subsequent fractions containing mixtures of the two isomers (total product 633 mg, 69%). An analytical sample of the major 1*R**,5*S** isomer was obtained by recrystallization from hexane to give plates of mp 104–105 °C.

IR ($CHCl_3$): 1645, 1570, 1470, 1450, 1385, 1300, 1285, 1270, 1135 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.64 (4 H, m), 5.92 (1 H, br s), 4.70 (1 H, m), 4.62 (1 H, s), 2.60 (1 H, m), 2.25–1.70 (3 H, m), 2.01 (3 H, m), 1.65 (3 H, s), 1.50 (3 H, s), 1.40 (1 H, dd, J = 14.8, 13.6 Hz). MS, *m/e* (%): 150 (2), 149 (39), 148 (4), 133 (5), 121 (43), 108 (6), 107 (100), 105 (9), 93 (16), 91 (6), 77 (6), 69 (12). Anal. Calcd for $C_{17}H_{21}{}^{79}BrO_2S$: MW 368.0446; C, 55.28; H, 5.73; Br, 21.64; S, 8.68. Found: MW 367.9862; C, 55.46; H, 5.83; Br, 21.81; S, 8.61.

(1*R,2*R**,4*S**)-2-Methyl-3-methylene-2-(phenylsulfonyl)bicyclo[2.2.1]hept-5-ene (31) and (1*R**,2*S**,4*S**)-2-Methyl-3-methylene-2-(phenylsulfonyl)bicyclo[2.2.1]hept-5-ene (30).** To a solution of sulfone **28a**[31] (176 mg, 0.72 mmol) in 4 mL THF at −78 °C was added dropwise a solution of 1.6 M *n*-butyllithium (500 μL, 0.80 mmol). This mixture was stirred for 40 min at this temperature and then neat methyl iodide (500 μL, 1.14 g, 0.83 mmol) was added. This mixture was allowed to come to room temperature during 1 h and then partitioned between 60 mL of ether and 15 mL of 10% sodium bisulfate. The organic layer was then extracted with 200 mL of saturated sodium bicarbonate, separated, and dried, and the solvent was removed in vacuo. The crude product was judged to be a 77:32 mixture of sulfones **31** and **30** based on integration of the ^{1}H NMR [an olefinic signal at δ 6.20 for **31** and at δ 6.31 for **30**]. The identity of the two isomers has been previously established.[15]

The sulfone **28b**[15] (178 mg, 0.72 mmol) was dissolved in 4 mL of THF and treated in a manner similar to that described above [also using *n*-butyllithium (500 μL, 0.80 mmol) and methyl iodide (500 μL, 1.14 g, 8.03 mmol)]. The crude alkylation product was judged to be a 77:23 mixture of **31** and **30**, the same ratio as that obtained from **28a**, so these crude products were combined and purified first by preparative TLC (1/1, hexane/ethyl acetate) to give 282 mg (76%) of a mixture of **31** and **30**. These two isomers were separated by preparative TLC using a freshly activated plate (baked at 110 °C for 2 h), and performing two elutions (5/1, hexane/ethyl acetate). This gave a mixture of 50 mg (13%) of **30** and 193 mg (52%) of **31** identified by a comparison of ^{1}H NMR data with that previously reported.[15]

(1*R,2*R**,4*S**)-2-Methyl-3-methylene-2-(phenylsulfonyl)-bicyclo[2.2.1]heptane (33) and (1*R**,2*S**,4*S**)-2-Methyl-3-methylene-2-(phenylsulfonyl)bicyclo[2.2.1]heptane (32).** To a solution of sulfone **29** (745 mg, 3.04 mmol) in 20 mL of THF at −78 °C was added dropwise a solution of 1.6 M *n*-butyllithium (2.0 mL, 3.2 mmol). The solution at first becomes light yellow, then becomes dark red during 1 h (solution allowed to warm to −50 °C). The solution was recooled to −78 °C and neat methyl iodide was added. The solution was gradually allowed to warm. No fading of the intense red color was noted until the mixture reached a temperature of between −55 and −50 °C. The solution was pale yellow at −30 °C. After further warming to room temperature during 1 h, this mixture was partitioned between 50 mL of ether and 50 mL of brine. The organic layer was separated and dried, and the solvent was removed in vacuo to give a crude yellow solid. Purification was accomplished by chromatography on a silica gel column (ethyl acetate/hexane gradient) to give 718 mg (90%) of a mixture of sulfones **32** and **33** in an 81:19 ratio as determined by integration of ^{1}H NMR [signal for **32** at δ 5.09 and for **33** at δ 5.14]. This mixture was a solid of undetermined melting point. The identity of the two isomers was determined by comparison with the ^{1}H NMR data reported by Veniard.[15]

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Synthesis and X-ray Crystallographic Characterization of an Oxo-Bridged Bimetallic Organosamarium Complex, $[(C_5Me_5)_2Sm]_2(\mu\text{-}O)$

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Abstract: $[(C_5Me_5)_2Sm]_2(\mu\text{-}O)$ is a common product in reactions of $(C_5Me_5)_2Sm(THF)_2$ with oxygen-containing substrates such as NO, N_2O, $CH_3CH_2\overline{CHCH_2O}$, or C_5H_5NO. The epoxide reaction, which liberates $CH_3CH_2CH{=}CH_2$ as a byproduct, gives the best yield, 55%. $[(C_5Me_5)_2Sm]_2(\mu\text{-}O)$ crystallizes from toluene/hexane under pentane diffusion at −3 °C in space group $I\bar{4}2m$ with unit cell dimensions a = 11.560 (5) Å, c = 14.236 (6) Å, and Z = 2 (dimers) for D_c = 1.50 g cm^{-3}. Least-squares refinement on the basis of 962 observed reflections led to a final R value of 0.036. The two $(C_5Me_5)_2Sm$ units of the dimer are connected by a linear Sm–O–Sm bridge with Sm–O distances of 2.094 (1) Å. The centroids of the four C_5Me_5 rings define a tetrahedron which surrounds the Sm–O–Sm unit. The C_5Me_5 rings are in an eclipsed conformation on each samarium. In contrast to the above oxidation reactions, $(C_5Me_5)_2Sm(THF)_2$ reacts with $OP(C_6H_5)_3$ to form the divalent adduct $(C_5Me_5)_2Sm[OP(C_6H_5)_3](THF)$.

The organometallic chemistry of the lanthanide metals in low oxidation states is currently undergoing rapid development. Investigations of both zero-valent metal-vapor chemistry and divalent metal-complex chemistry have led to a variety of new classes of

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