Phenylsulfonyl as a β Participating Group

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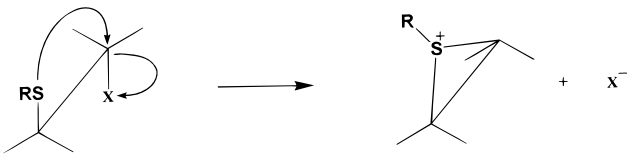
The phenylsulfonyl group ($PhSO_2$) has been examined for its β effect properties. The stereochemical relationship was varied between phenylsulfonyl and a nucleophilic leaving group (nucleofuge) separated by two carbons. Mechanisms were distinguished through solvent effects on rates and products. When the stereochemistry between the two groups was gauche, the only effect of phenylsulfonyl was strong inductive retardation in a mechanism involving solvent participation. With the antiperiplanar stereochemistry, however, the mechanism clearly changed to carbocation formation with a small kinetic acceleration. Thus, phenylsulfonyl is a weak β effect substituent. This remarkable property for a strongly electron-withdrawing group occurs most likely through hyperconjugation or possibly through anchimeric assistance.

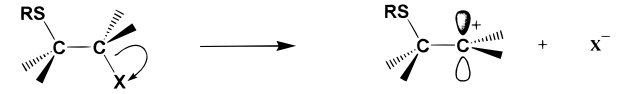
Sulfur in its divalent state has been thoroughly studied as an intramolecular nucleophile in neighboring group participation (Scheme 1).[1] The favorable properties of sulfur in this context result from the available coordination sites through the lone electron pairs and from the large size and polarizability of sulfur and its consequent high nucleophilicity. Sulfur has never been studied as a β effect atom capable of acting through hyperconjugation. The distinction to be made is that in neighboring group participation (anchimeric assistance, Scheme 1) sulfur displaces the leaving group by a traditional intramolecular S_N2 mechanism (Traylor's nonvertical participation[2]), whereas in the alternative β effect mechanism the role of the substituent is to provide hyperconjugation for stabilization of a carbocation formed in an S_N1 reaction (vertical participation) (see Scheme 2). Vertical participation (only an approximate descriptor but a useful one nonetheless[2]) has been widely studied with silicon or other group 14 elements as the β effect atom.[3] These atoms all possess lower electronegativity than carbon and, hence, are clearly electron donors. They differ from sulfur in that they do not possess lone pairs, so that the nonvertical mechanism, analogous to Scheme 1, must involve σ rather than lone pair electrons.

The β effect has been little studied outside of group 14, although recently evidence has been reported for various phosphorus functionalities in group 15.[4] There is no experimental evidence concerning the phosphine functionality (H_2P as the β effect group), but calculations indicated that the β effect of phosphine is comparable to that of trimethylsilyl.[4] There was experimental support that thiophosphinoyl ($Ph_2(S{=})P$) exhibits a strong β effect, phosphinoyl ($Ph_2(O{=})P$) is modest, and phosphonate ($(EtO)_2(O{=})P$) is weak. The β effects of these three functionalities also were substantiated by theory.[4]

Scheme 1



Scheme 2



The weakening of the effect for the higher oxidation states of phosphorus is caused by the increased electron deficiency of the substituent as electronegative atoms are added. Thus, a balance is struck between the inductive and hyperconjugative effects. Silicon, germanium, tin, and phosphorus groups without electronegative substituents, e.g., Me_3Si and H_2P, exhibit strong β effect properties, but more electronegative substituents, e.g., Cl_3Si and $(EtO)_2(O{=})P$, decrease or quench the effect.[4,5] Thiophosphinoyl and phosphinoyl still exhibit strong residual β effect properties: (1) rate acceleration associated with the antiperiplanar stereochemistry between the β atom and the leaving group X (analogous to Scheme 2), (2) change in mechanism from solvent assistance for the gauche stereochemistry to a free carbocation intermediate for the antiperiplanar stereochemistry (vertical participation is nearly eliminated in the gauche stereochemistry), (3) isotope effects characteristic of a carbocation as in Scheme 2 rather than a closed structure as in Scheme 1, and (4) product structures consistent with carbocation formation rather than solvent assistance.[2,3]

We are now moving our focus to sulfur in group 16. We begin with an examination of the sulfonyl functionality, to avoid ambiguities that are inherent in the sulfide group, which can readily undergo internal displacements as in Scheme 1. There is no reported evidence to our knowledge that sulfonyl can serve as an internal nucleophile. The sulfur atom does not possess lone pairs and hence cannot serve as a nucleophile. It is still possible

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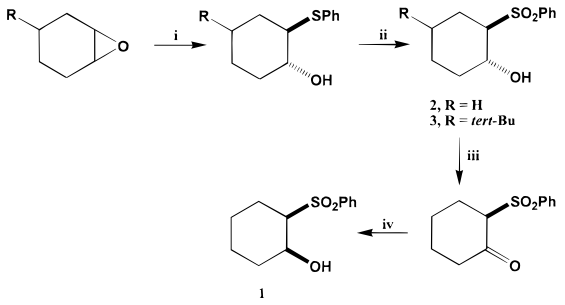
Scheme 3[a]

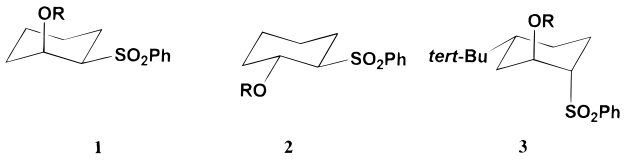


[a] Key: (i) PhSH, NaOH, heat; (ii) H_2O_2, CH_3CO_2H; (iii) pyridinium chlorochromate; (iv) L-Selectride.

for the oxygen atoms to be nucleophiles, in which case a four-membered ring would be formed. The oxygen atoms increase the electronegativity of the substituent, just as with the phosphinoyl group. To explore the possibility of β effect activity of the sulfonyl group, we have synthesized molecules respectively with gauche and antiperiplanar relationships between sulfur and the leaving group. The gauche molecule serves as a model for reaction without vertical assistance, and the antiperiplanar molecule is the target to determine whether sulfonyl is a β effect group.

Results

Molecules **1**−**3** permit examination of vertical participation of the sulfonyl functionality. The dihedral angle



1 **2** **3**

between the cis or gauche substituents in **1** is approximately 60°, which permits very little hyperconjugation. The dihedral angle in the biased trans (antiperiplanar) system **3** is approximately 180°, which is ideal for hyperconjugation. The unbiased trans case **2** is free to interconvert between gauche and antiperiplanar forms. The *A* values of hydroxy and phenylsulfonyl respectively are 0.87 (hydroxylic solvents) and 2.5.[6] Consequently, the cis system **1** exists preferentially in the gauche conformation shown (rather than in the conformation with phenylsulfonyl axial and hydroxy equatorial), and the unbiased trans system **2** exists preferentially in the gauche diequatorial conformation shown (rather than the antiperiplanar diaxial form).

These molecules were synthesized according to literature analogies.[7] Cyclohexene oxide was treated with thiophenoxide to produce *trans*-2-hydroxycyclohexyl phenyl sulfide, which was oxidized to **2** (R = H) with hydrogen peroxide (Scheme 3). Treatment of **2** with pyridine chlorochromate produced the ketone, which was reduced with L-Selectride to **1** (R = H). The biased form **3** (R = H) was analogously produced from *trans*-4-*tert*-butylcyclohexene oxide.[8] The alcohols (**1**−**3**, R = H) were converted to their triflates for kinetic studies (**1**−**3**, R = SO_2CF_3 or Tf). The rates of the analogous tosylates were unmeasurably slow because of the stronger electron-withdrawing effect of the sulfonyl groups compared with any of the phosphorus groups. Only the triflates exhibited rates that could be measured conductometrically. As we examine rate ratios and changes with solvent rather than absolute numbers, leaving group differences tend to cancel out within a constant mechanism.

Table 1. Rate Constants for Triflates

substrate	solvent[a]	*T*, °C	rate, s^{-1}
1 (cis)	97% TFE	40.0	1.62×10^{-4}
		35.0	7.46×10^{-5}
		31.5	5.86×10^{-5}
		25.0	2.39×10^{-5}[b]
	80% TFE	40.0	7.03×10^{-4}
	60% TFE	40.0	1.20×10^{-3}
	80% EtOH	40.0	7.33×10^{-4}
	70% EtOH	40.0	8.18×10^{-4}
	60% EtOH	40.0	1.32×10^{-3}
2 (unbiased trans)	97% TFE	40.0	4.29×10^{-4}
		35.0	2.28×10^{-4}
		30.5	1.24×10^{-4}
		25.0	5.86×10^{-5}[b]
	80% TFE	40.0	9.98×10^{-4}
	60% TFE	40.0	1.87×10^{-3}
	80% EtOH	40.0	8.39×10^{-4}
	70% EtOH	40.0	8.61×10^{-4}
	60% EtOH	40.0	2.05×10^{-3}
3 (biased trans)	97% TFE	40.0	2.39×10^{-3}
		35.0	1.39×10^{-3}
		30.0	7.60×10^{-4}
		25.0	4.20×10^{-4}
	80% TFE	35.0	2.21×10^{-3}
	60% TFE	35.0	1.48×10^{-3}
	80% EtOH	35.0	2.29×10^{-4}
	70% EtOH	35.0	5.24×10^{-4}
	60% EtOH	35.0	3.53×10^{-4}

[a] Percentages are weight/weight for trifluoroethanol (TFE) and volume/volume for ethanol (EtOH). [b]Calculated from rates at other temperatures.

Table 2. Activation Parameters in 97% TFE at 25.0 °C

substrate	E_a, kcal mol^{-1}	log *A*	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal deg^{-1} mol^{-1}	$\Delta G^{\ddagger}$, kcal mol^{-1}
1	23.0	12.19	22.4	−2.8	23.2
2	24.7	13.85	24.1	2.8	23.2
3	21.6	12.46	21.0	−3.6	22.1

Kinetics were carried out in a variety of solvents and at multiple temperatures in order to define the reaction mechanism through its sensitivity to solvent properties. The kinetic results are given in Table 1 and the activation parameters in Table 2. The rates in all the solvents are plotted against the analogous rates for 1-adamantyl bromide in the manner of Raber, Harris, and their coworkers[9] (Figures 1−3). Product studies were carried out in 97% trifluoroethanol and 80% ethanol for a gauche and an anti case. Products were largely from elimination (**4**, **5**) with some substitution (**6**), as detailed in Table 3.

Discussion

Rates were measured in multiple solvent mixtures in order to determine whether the reaction rate was sensi-

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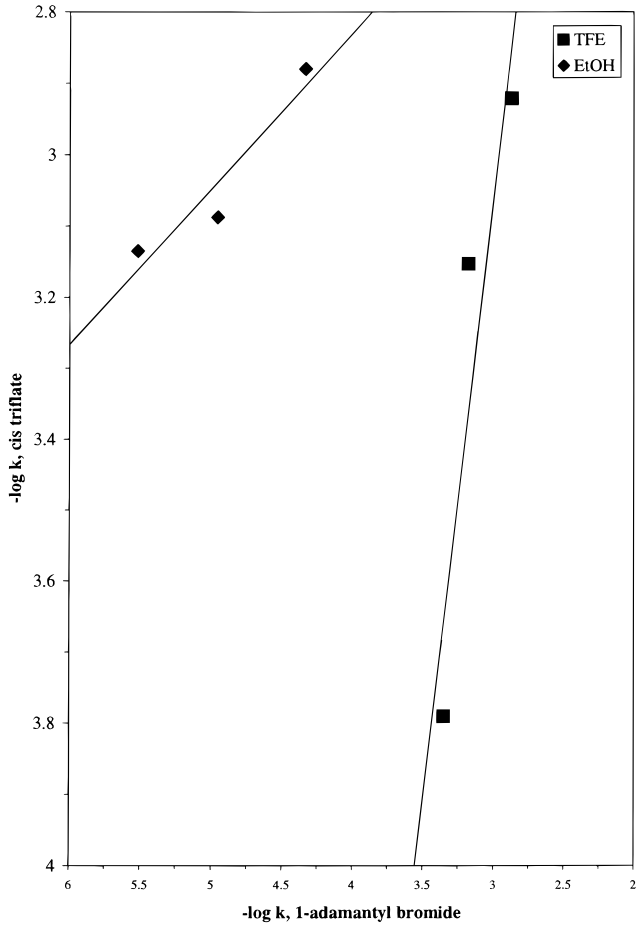


Figure 1. Raber−Harris plot of *cis*-2-(trifluoromethanesulfonyl)cyclohexyl phenyl sulfone (**1-OTf**).

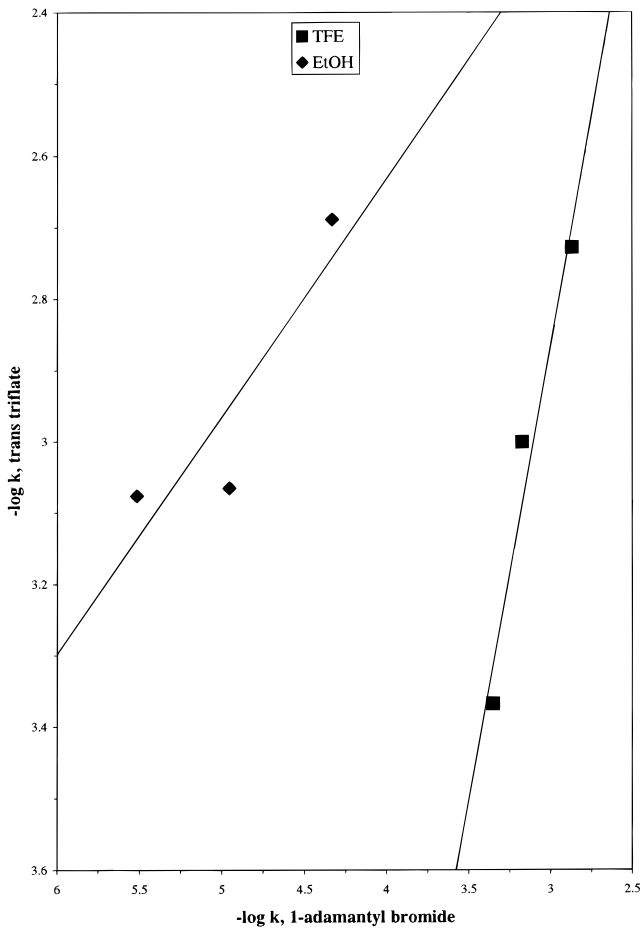


Figure 2. Raber−Harris plot of *trans*-2-(trifluoromethanesulfonyl)cyclcohexyl phenyl sulfone (**2-OTf**).

tive to solvent nucleophilicity or to ionizing power. A mechanism in which the solvent attacks the substrate would be sensitive to nucleophilicity, whereas one involving ionization to a carbocation would be sensitive to ionizing power. Carbocation formation is required for involvement of hyperconjugation. Raber, Harris, and their co-workers[9] developed a method for drawing this distinction by taking advantage of the differences between aqueous mixtures of ethanol or trifluoroethanol. Higher proportions of water in ethanol increase solvent ionizing power with little change in solvent nucleophilicity, whereas higher proportions of water in trifluoroethanol have the opposite effect, increasing solvent nucleophilicity with little change in ionizing power.

These authors illustrated the differences by plotting the rates of a selected substrate against those of 1-adamantyl bromide, which reacts by a carbocation mechanism.[9] When the substrate also reacts by a carbocation mechanism (S_N1 or E1, also called k_C), both axes of the plot are responding to similar phenomena and the plot is linear. When the substrate involves solvent in the transition state (S_N2 or E2, also called k_s), two separate lines are observed, respectively, for the ethanol and trifluoroethanol data, as the solvent mixtures respond in different ways to the different mechanisms. The ethanol points tend to spread out along the *x* axis as the adamantyl rate (k_C) varies with ionizing power, and the trifluoroethanol points tend to spread out along the *y* axis as the substrate rate (k_s) varies with nucleophilicity.

As Figure 1 shows, the cis substrate (**1**, R = Tf) is a typical nucleophilic (k_s) substrate, giving a two-line Raber−Harris plot. The trifluoroethanol rates are spread out along the *y* axis over almost 1 order of magnitude, reflecting sensitivity to solvent nucleophilicity, whereas the ethanol rates vary by only about 20%, reflecting little sensitivity to ionizing power. In the cis stereochemistry, there is no opportunity for hyperconjugation because of the gauche relationship between the sulfonyl substituent and the leaving group. As Figure 2 illustrates, the situation is essentially identical for the unbiased trans substrate **2** (R = Tf). The sulfonyl group apparently holds the molecule in the diequatorial form with the gauche relationship between groups.

The biased trans substrate **3** (R = Tf), however, exhibits a classic one-line plot, characteristic of a carbocation (k_C) mechanism. The rates have slowed in trifluoroethanol, raising them above all the ethanol points in the negative log plot. Because both the substrate on the *y* axis and the standard on the *x* axis react by the same carbocation mechanism, the trifluoroethanol points, reflecting little or no sensitivity to solvent nucleophilicity, bunch together. The result is a single line. This same behavior was observed for the antiperiplanar thiophosphinoyl ($Ph_2(S{=})P$), phosphinoyl ($Ph_2(O{=})P$), and phosphonate ($(EtO)_2(O{=})P$) substrates,[4] all of which contain electron-withdrawing groups. Similar to these substituents, phenylsulfonyl ($PhSO_2$) changes the mechanism from solvent assistance in the gauche stereochemistry to carbocation in the antipiplanar stereochemistry.

It is quite remarkable that a carbocation can be

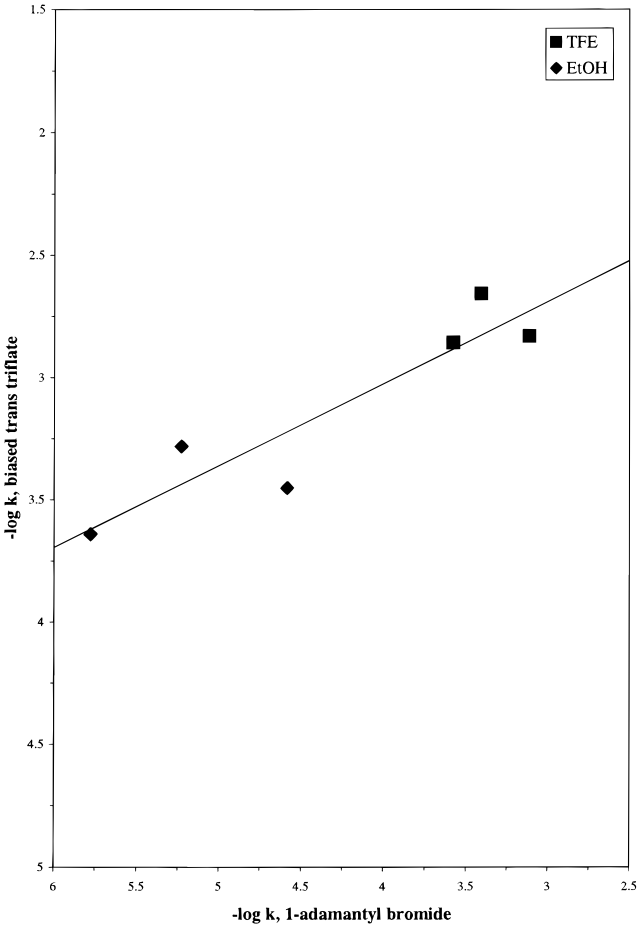
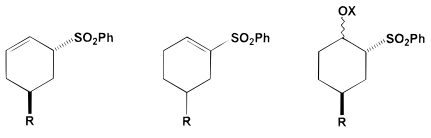


Figure 3. Raber−Harris plot of *trans*-2-(trifluoromethanesulfonyl)-4-*tert*-butylcyclohexyl phenyl sulfone (**3-OTf**).

Table 3. Product Studies (%)

substrate	product	97% TFE	80% EtOH
2	**6**, R = H, X = CH_2CF_3	40	76
	4, R = H	53	2
	5, R = H	7	
	6, R = H, X = Et		18
3	**4**, R = *t*-Bu	17	49
	5, R = *t*-Bu	71	29
	6, R = *t*-Bu, X = H		9



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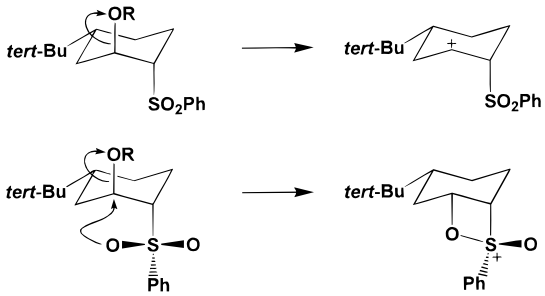
generated in the presence of the strongly electron-withdrawing phenylsulfonyl group. It is expected that the change in mechanism must be accompanied by a rate enhancement. The biased trans to cis rate ratio (Table 1) in 97% trifluoroethanol at 25 °C is 17.6. The analogous ratios for the diethylphosphonate, diphenylphosphinoyl, and diphenylthiophosphinoyl groups[4] are 12.7, 440, and 3.2×10^6, respectively (all of these substituents show one-line Raber−Harris plots for the biased trans forms and two-line plots for the cis forms). Thus, sulfonyl is comparable to phosphonate in its ability to stabilize a carbocation: weak but still effective. These rate ratios may not be entirely comparable, however, as triflate is the leaving group for sulfonyl but tosylate was used for the phosphonate.[4]

Scheme 4



The products from the trans substrates substantiate the change in mechanism between the unbiased and biased forms. Unbiased **2** gives a mix of substitution and elimination, typical for reaction with solvent participation. Moreover, the predominant elimination product in the more ionizing solvent 97% trifluoroethanol contained the sulfonyl group allylic to the double bond, **4**. This structure is easily obtained from **2** by E2 elimination of the 3 proton and the 2 leaving group (OSO_2CF_3). Biased **3**, on the other hand, gives as the predominant elimination product the isomer with the sulfonyl group attached to the double bond, **5**. The eliminated proton is geminal to the sulfonyl group and syn to the 2 leaving group. Given that syn elimination presumably is unlikely, the higher proportion of the nonallylic isomer **5** is impossible in a bimolecular reaction (k_s) such as participation (E2) and is consistent with carbocation formation k_C (E1). Thus, the product structures corroborate the kinetic results. All of the products retained the sulfonyl group; i.e., there is no fragmentation in which $PhSO_2$ rather than a proton is the electrofuge. Such a pathway normally is indicative of considerable positive charge on the electrofuge and is common in the β effect reactions of silicon.[3] Its absence is consistent with sulfonyl as only a weakly hyperconjugating group.

Conclusions

Phenylsulfonyl is a weak β effect group when positioned antiperiplanar to an excellent nucleofuge such as triflate in a strongly ionizing solvent such as 97% trifluoroethanol. This stereochemistry is offered only by the biased trans substrate **3**. The β effect activity is substantiated by the one-line Raber−Harris plot (Figure 3) indicative of a carbocation mechanism, by the modest rate acceleration of 17.6 for the biased trans form **3** compared with the cis form **1**, and by predominant formation of the syn elimination product **5**.

There is still the question as to whether phenylsulfonyl is operating as a typical β effect group through hyperconjugation, analogous to Scheme 2, or as an internal nucleophile analogous to Scheme 1. The two possibilities are illustrated in Scheme 4. In the standard vertical process shown at the top, departure of the nucleofuge is assisted by hyperconjugative stabilization by the β bond, in this case C−SO_2Ph. The high polarizability of the sulfonyl group must overcome the strong inductive electron withdrawal. In an unprecedented nonvertical process shown at the bottom, sulfonyl serves as an internal nucleophile to form a four-membered ring. The Raber−Harris plot and the product structures are more in agreement with the vertical mechanism, whereas the rate acceleration is consistent with either. We cannot

make a definitive mechanistic assignment, although by analogy with the phosphorus cases we lean toward vertical stabilization through C−SO_2Ph hyperconjugation.

The weak ability of sulfonyl to stabilize a β carbocation, documented herein for the first time, now complements the well-known ability of sulfonyl to stabilize an α carbanion.[10]

Experimental Section

***trans*-2-Hydroxycyclohexyl Phenyl Sulfide.** A dried, 500 mL, round-bottomed flask, equipped with a metallic stirring bar and a reflux condenser, was charged with thiophenol (13.66 g, 124.0 mmol), NaOH (5.45 g, 136.3 mmol), and CH_3OH (200 mL). The mixture was stirred for 5 min, at which time cyclohexene oxide (16.55 g, 168.6 mmol) was added. This whitish, cloudy mixture was stirred and heated to reflux for 4 h. The golden liquid product was then cooled, and the CH_3OH solvent was removed by rotary evaporation to give a thick golden liquid. This liquid was dissolved in ether (150 mL), placed in a separatory funnel, and washed with 2 M NaOH. The cloudy organic layer was collected and dried ($MgSO_4$). The drying agent was filtered off to give a clear, colorless solution. The ether solvent was removed by rotary evaporation to give a thick, off-white, liquid product (25.53 g, 122.5 mmol, 99%), which was carried on to the next step without purification.

***trans*-2-Hydroxycyclohexyl Phenyl Sulfone (2-OH).** A 250 mL beaker was charged with *trans*-2-hydroxycyclohexyl phenyl sulfide (14.17 g, 68.02 mmol), 30% H_2O_2 (30 mL), and glacial acetic acid (30 mL). This white, cloudy, thick liquid was placed on a boiling water bath and heated for 6.5 h. After this time, the beaker contained a thick, colorless liquid, which was left open in the hood overnight to form a cake of white solid. This crude material (17.69 g, 73.63 mmol, 108%) still smelled of acetic acid. The solid was recrystallized using a mixed solvent system of $CHCl_3$ and hexane. The solution was cooled to room temperature, and white crystals appeared. Vacuum filtration was used to collect and dry the long, white, crystalline sulfone (16.81 g, 69.93 mmol, 100%): mp 106−107 °C; ^{1}H NMR ($CDCl_3$) δ 1.15−1.45 (m, 4H), 1.60−1.80 (dd, 2H), 1.87−1.95 (dd, 1H), 2.10−2.20 (m, 1H), 2.50−2.71 (br s), 2.90−3.10 (m, 1H), 3.90−4.00 (dt, 2H), 7.52−7.80 (m, 3H), 7.88−7.98 (d, 2H); ^{13}C NMR ($CDCl_3$) δ 23.5, 24.4, 25.6, 34.1, 68.2, 68.8, 128.9, 129.2, 134.1, 136.6. Anal. Calcd for $C_{12}H_{16}SO_3$: C, 59.97; H, 6.71. Found: C, 59.87; H, 6.77.

***trans*-2-(Trifluoromethanesulfonyloxy)cyclohexyl Phenyl Sulfone (2-OTf).** A 25 mL, round-bottomed flask was charged with trifluoromethanesulfonic anhydride (0.65 mL, 1.09 g, 3.86 mmol) in CCl_4 (8 mL), a magnetic stir bar, a rubber septum, and an N_2 inlet syringe. This solution was stirred and chilled on an ice bath for 5 min. A solution of *trans*-2-hydroxycyclohexyl phenyl sulfone (0.20 g, 0.796 mmol) and pyridine (0.30 g, 3.79 mmol) in CCl_4 (10 mL) and CH_2Cl_2 (1 mL) was added to the stirred anhydride solution by syringe. This cloudy mixture was stirred and chilled for 4 h. At this time, it was sealed with Parafilm and placed in a refrigerator. A sample of the reaction mixture was removed each day by syringe; the solvent was removed, the resultant solid was dissolved in $CDCl_3$, and the sample was analyzed by ^{1}H NMR. The sample was then returned to the reaction vessel by syringe. The spectrum showed the reaction had gone to completion after 9 days. The reaction mixture was then removed from the refrigerator, washed with H_2O, dried ($MgSO_4$), filtered, and concentrated to give a peach-brown, powdery solid (0.19 g, 0.51 mmol, 64%): ^{1}H NMR ($CDCl_3$) δ 1.25−2.51 (m, 9H), 2.30−2.45 (m, 1H), 3.30−3.40 (q, 1H), 5.30−5.39 (m, 1H), 7.55−7.70 (dt, 3H), 7.88−7.92 (d, 2H); ^{13}C NMR ($CDCl_3$) δ 21.4, 22.0, 23.7, 30.6, 64.2, 76.7, 77.1, 77.5, 128.8, 129.5, 134.3, 137.9.

2-Oxocyclohexyl Phenyl Sulfone. A 250 mL, round-bottomed flask was charged with pyridinium chlorochromate (PCC, 4.08 g, 18.93 mmol) in CH_2Cl_2 (100 mL), a magnetic stir bar, a Claisen adapter fitted with a reflux condenser, an N_2 inlet, and a dropping funnel. The dropping funnel was charged with *trans*-2-hydroxycyclohexyl phenyl sulfone (2.39 g, 9.94 mmol) in CH_2Cl_2 (50 mL). The clear, colorless solution was added to the bright orange suspension of PCC, causing an immediate color change to dark brown while foaming. The mixture was left to stir overnight. After this time, the orange-brown reaction mixture was diluted with ether (40 mL), and the cloudy orange liquid was decanted off of the black, tarry solid. This material, after being washed with ether (3 × 30 mL), turned into a granular black solid. All of the ether layers were combined and passed through a column of Florisil (20 g), which was then washed with ether. The combined light green ether portions were concentrated by rotary evaporation to give a light green, powdery solid product (1.90 g, 7.97 mmol, 80%), which was used in the next step without purification.

***cis*-2-Hydroxycyclohexyl Phenyl Sulfone (1-OH).** 2-Oxocyclohexyl phenyl sulfone (0.915 g, 3.807 mmol) was dissolved in dry THF (30 mL). This clear, very pale yellow solution was stirred and cooled on an ice bath for 5 min, at which time L-Selectride (lithium tri-*sec*-butylborohydride, 1.0 M in THF, 8 mL, 8 mmol) was added via syringe. Upon addition, the solution turned to a slightly darker yellow, which then faded back to a lighter hue. The solution was cooled and stirred for 1 h 10 min. After this time, the yellow solution was opened to the air and quenched with dropwise addition of H_2O (4 mL) until foaming upon addition ceased. The solution was then removed from the ice bath, and a solution of 30% H_2O_2 (8 mL) and 2 M NaOH (30 mL) was added. The resultant two-layered solution was diluted with H_2O (20 mL) and transferred to a separatory funnel. The organic layer was drained off, and the aqueous layer was washed with ether. The combined organic layers were dried (Na_2SO_4), and the drying agent was filtered off. The solvent was evaporated to give a thick colorless liquid, which was then pumped by vacuum to give a white powdery crude solid (0.407 g, 1.64 mmol, 43%). Analysis by NMR showed this crude mixture to be predominantly the cis sulfone product with a very small amount of contaminating trans sulfone. This solid was recrystallized using a mixed solvent system of $CHCl_3$ and hexane to give an isolated white crystalline solid of pure cis sulfone product (0.17 g, 0.707 mmol, 19%): mp 95−96 °C; ^{1}H NMR ($CDCl_3$) δ 1.15−1.35 (m, 2H), 1.40−1.50 (dd, 1H), 1.68−2.12 (m, 5H), 2.10−2.20 (m, 1H), 2.87−2.95 (dt, 1H), 3.30−3.38 (s), 4.27−4.32 (s, 1H), 7.55−7.75 (m, 3H), 7.90−7.95 (dd, 2H); ^{13}C NMR ($CDCl_3$) δ 18.5, 19.0, 24.9, 32.2, 63.4, 66.1, 128.6, 129.3, 134.0, 141. Anal. Calcd for $C_{12}H_{16}SO_3$: C, 59.97; H, 6.71. Found: C, 60.38; H, 6.38.

***cis*-2-(Trifluoromethanesulfonyloxy)cyclohexyl Phenyl Sulfone (1-OTf).** A solution of triflic anhydride (0.96 g, 3.39 mmol) in 10 mL of CH_2Cl_2 was added to a solution of *cis*-2-hydroxycyclohexyl phenyl sulfone (**1-OH**) (0.8 g, 2.83 mmol) and pyridine (0.47 g, 5.95 mmol) in 10 mL of CH_2Cl_2 at 0 °C. The solution was stirred for 3 h and then diluted with 10 mL of CH_2Cl_2, washed with H_2O at 0 °C, and dried ($MgSO_4$). Removal of the solvent by rotary evaporation afforded the triflate, which was recrystallized as a white solid: ^{1}H NMR ($CDCl_3$) δ 7.96−7.55 (m, 5), 5.76−5.70 (dd, 1), 3.12−3.05 (m, 1), 2.48−2.41 (m, 1), 2.04−1.10 (m, 7); ^{13}C NMR ($CDCl_3$) δ 18.93, 21.37, 24.08, 31.28, 65.47, 81.65, 129.04, 129.44, 132.27.

***trans*-4-(*tert*-Butyl)cyclohexene oxide** was prepared as before.[4,8]

***trans*-2-Hydroxy-4-*tert*-butylcyclohexyl Phenyl Sulfide.** A dried, 50 mL, round-bottomed flask containing a metallic stirring bar and a reflux condenser was charged with thiophenol (1.02 g, 9.26 mmol), NaOH (0.38 g, 9.48 mmol), and CH_3OH (25 mL). This mixture was stirred for 5 min, at which time *trans*-4-*tert*-butylcyclohexene oxide (1.18 g, 7.50 mmol) was added to the reaction flask. This cloudy mixture was stirred and heated to reflux for 1.5 h. At this point, the mixture was cooled to room temperature and concentrated by rotary evaporation to give 4.00 g of a light yellow thick liquid. This liquid was washed into a separatory funnel with ether (30 mL).

(10) Gais, H.-J.; van Gampel, M.; Raabe, G.; Müller, J.; Braun, S.; Lindner, H. J.; Rohs, S.; Runsink, J. *Eur. J. Org. Chem.* **1999**, 1627−1651.

The ether was washed with 2 M NaOH. The resultant organic layer was dried ($MgSO_4$), the drying agent was filtered off, and the liquid was concentrated to give a cloudy thick liquid product (1.02 g, 3.87 mmol, 52%): ^{1}H NMR ($CDCl_3$) δ 0.84 (s, 9H), 1.31−1.90 (m, 8H), 2.10−2.20 (m, 1H), 4.15 (s, 1H), 7.17−7.35 (m, 3H), 7.36−7.45 (d, 2H).

***trans*-2-Hydroxy-4-*tert*-butylcyclohexyl Phenyl Sulfone (3-OH).** A 100 mL beaker was charged with *trans*-2-hydroxy-(4-*tert*-butylcyclohexyl) phenyl sulfide (1.02 g, 3.87 mmol), acetic acid (2.52 g), and 30% H_2O_2 (2.60 g). This mixture was heated on a water bath for 3 h. The thick, yellowish liquid (1.02 g) that resulted was dissolved in ether (50 mL) and extracted with H_2O. The organic layer was dried (Na_2SO_4) and concentrated to give an off-white solid (0.31 g). NMR and TLC of this material showed a mixture of components, which were further separated by column chromatography using a solvent system of 60% hexane and 40% ethyl acetate. The chromatography products were combined, and the solvent was removed by rotary evaporation to give a white solid sulfone product (0.25 g, 0.85 mmol, 22%): mp 106−108 °C; ^{1}H NMR ($CDCl_3$) δ 0.85 (s, 9H), 1.36−1.98 (m, 8H), 3.17 (m, 1H), 4.52 (m, 1H), 7.52−7.70 (m, 3H), 7.89 (d, 2H); ^{13}C NMR ($CDCl_3$ δ 20.8, 21.6, 27.3, 30.8 32.3, 39.6, 64.9, 128.5, 129.2, 133.7, 138.1. Anal. Calcd for $C_{16}H_{24}SO_3$: C, 64.83; H, 8.16. Found: C, 64.20; H, 8.00

***trans*-2-(Trifluoromethanesulfonyloxy)-4-*tert*-butylcyclohexyl Phenyl Sulfone (3-OTf).** A 25 mL, round-bottomed flask was charged with trifluoromethanesulfonic anhydride (0.20 mL, 1.01 mmol) in CCl_4 (10 mL), a magnetic stirring bar, a rubber septum, and an N_2 inlet syringe. This solution was stirred and chilled on an ice bath for 5 min. At this time, a solution of *trans*-2-hydroxy-(4-*tert*-butylcyclohexyl)phenyl sulfone (0.10 g, 0.337 mmol) and pyridine (0.22 g, 2.78 mmol) in CCl_4 (10 mL) and CH_2Cl_2 (2 mL) was added to the stirring anhydride solution by syringe. This cloudy mixture was stirred and chilled for 1 h. At this time, it was sealed with Parafilm and placed in a freezer. A sample of the reaction mixture was removed each day by syringe; the solvent was removed, the resultant solid was dissolved in $CDCl_3$, and the sample was analyzed by ^{1}H NMR. The sample was then returned to the reaction vessel by syringe. The spectrum showed the reaction had gone to completion after 15 days. The reaction mixture was then removed from the refrigerator, washed with H_2O, dried ($MgSO_4$), filtered, and concentrated to give a light red-brown, powdery solid (0.03 g, 0.07 mmol, 21%): ^{1}H NMR ($CDCl_3$) δ 0.90−1.00 (m, 9H), 1.30 (s, 1H), 1.45−1.55 (m, H), 1.71−2.40 (m, 6H), 3.45−3.50 (d, 1H), 5.61−5.65 (s, 1H), 7.61−7.81 (dt, 3H), 7.93−7.98 (d, 2H); ^{13}C NMR ($CDCl_3$) δ 20.9, 21.0, 27.1, 29.7, 32.1, 40.0, 62.2, 76.7, 77.1, 77.6, 84.5, 128.5, 129.7, 134.5, 137.6

Product studies and kinetic studies were carried out as before,[4] although all kinetics were determined conductometrically.

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