Iodosulfonation of alkenes with benzenesulfinic acid – *N*-iodosuccinimide — Facile preparation of α,β-unsaturated sulfones[1]

Russell R. Wolff, Vikram Basava, Robert M. Giuliano, Walter J. Boyko, and J. Herman Schauble

Abstract: Reaction of alkenes and alkenols with *N*-iodosuccinimide (NIS) and benzenesulfinic acid in dichloromethane at room temperature affords *vic*-iodophenylsulfonyl adducts in good to high yields. Treatment of the iodosulfones with neutral alumina in dichloromethane at room temperature results in dehydroiodination to give the corresponding vinyl sulfones in high yield and purity by this convenient two-step procedure. Application of the iodosulfonation–dehydroiodination sequence to allylic alcohols and silyl ethers gave γ-oxygenated, α,β-unsaturated phenylsulfones, while the attempted iodosulfonation of glycals, as intermediates to vinyl sulfones, resulted in addition of benzenesulfinic acid with double bond shift (Ferrier rearrangement).

Key words: iodosulfonation, vinyl sulfones, benzenesulfinic acid, *N*-iodosuccinimide, dehydroiodination.

Résumé : La réaction d'alcènes et d'alcénols avec du *N*-iodosuccinimide (NIS) et de l'acide benzènesulfinique dans le dichlorométhane à la température ambiante conduit à la formation d'adduits *vic*-iodophénylsulfonyles avec des rendements allant de bons à élevés. Le traitement des iodosulfones avec de l'alumine neutre dans le dichlorométhane à la température ambiante provoque une déshydroiodation qui fournit les vinylsulfones correspondantes avec un rendement et une pureté élevés et qui complète cette méthode de synthèse pratique en deux étapes. L'application de la séquence de réactions iodosulfonation–déshydroiodation à des alcools allyliques et à des éthers silylés conduit à la formation de phénylsulfones γ-oxygénées et α,β-insaturées alors que les essais d'iodosulfonation de glycals, pour conduire à des intermédiaires de vinyl sulfones, conduisent à une addition de l'acide benzènesulfinique avec un déplacement de la double liaison (réarrangement de Ferrier).

Mots clés : iodosulfonation, vinyl sulfones, acide benzènesulfinique, *N*-iodosuccinimide, déshydroiodation.

[Traduit par la Rédaction]

Introduction

The two-step halosulfonation–dehydrohalogenation sequence is a useful method for conversion of alkenes to α,β-unsaturated sulfones. The first step of this process has generally been carried out by the reaction of an alkene with an arylsulfonyl halide to give a *vic*-halo(arylsulfonyl)alkane (1). Such reactions with sulfonyl chlorides or bromides occur via a radical-chain process, and require initiators such Cu(I, II) (2–5) or Ru(II) (6) salts, peroxides (7–9), or UV irradiation (5, 8, 10, 11).

Arylsulfonyl iodides are considerably more susceptible to homolysis than the chlorides, typically undergoing slow addition to alkenes in the dark (12, 13), although being accelerated by ambient or applied visible light (12–16), Cu(II) salts (17), or other radical initiators (12). Arylsulfonyl iodides are unstable reagents that are prepared from iodine and sodium arylsulfinate. Direct iodosulfonation can also be carried out with iodine and sodium arylsulfinate; however, a catalyst, such as a Cu(II) or Hg(II) salt, is usually included (18–20).

Herein we describe an alternate synthesis of iodo(arylsulfonyl)alkanes by the reaction of alkenes with *N*-iodosuccinimide (NIS) and benzenesulfinic acid in dichloromethane at room temperature. The free sulfinic acid is soluble in organic solvents, and is stable for extended periods when stored at 0 °C. Iodophenylsulfonyl adducts are obtained regioselectively in good yields. We also report that treatment of the iodosulfones with neutral alumina at room temperature results in facile elimination of HI, to give synthetically useful vinyl sulfones in high yield and purity.

Results and discussion

Iodosulfonation products obtained from reaction of various alkenes and alkenols with NIS and benzenesulfinic acid are listed in Table 1. Reactions of cyclopentene, cyclohexene, 1-methylcyclohexene, and norbornylene all gave high

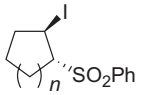
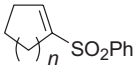
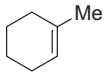
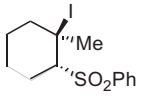
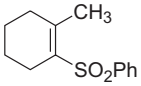
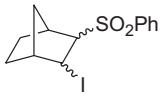
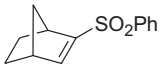
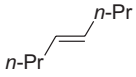
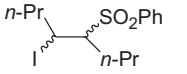
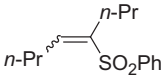
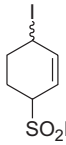
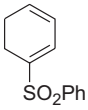
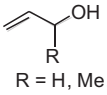
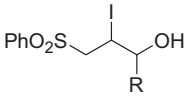
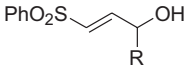
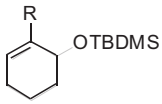
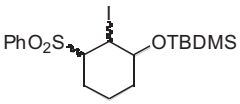
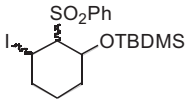
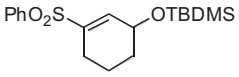
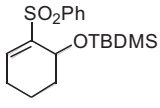
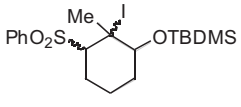
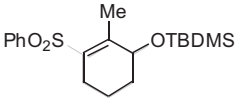
Received 30 August 2005. Published on the NRC Research Press Web site at http://canjchem.nrc.ca on 17 May 2006.

R.R. Wolff, V. Basava, R.M. Giuliano,[2] W.J. Boyko, and J.H. Schauble. Department of Chemistry, Villanova University, Villanova, PA 19085, USA.

[1]This article is part of a Special Issue dedicated to Professor Walter A. Szarek.
[2]Corresponding author (e-mail: robert.giuliano@villanova.edu).

 doi:10.1139/V06-051

Table 1. Iodophenylsulfonylation of alkenes using NIS – benzenesulfinic acid and dehydroiodination of iodo(henylsulfonyl) compounds on neutral alumina.

Alkene	Iodosulfonylation Product	Yield[a]	Dehydroiodination Product	Yield[b]
 *n* = 1, 2	 **1** *n* = 1 **3** *n* = 2	91% 86% (73%)[c]	 **2** *n* =1 **4** *n* = 2	92% 95% (83%)[c]
	 **5**	90%[d]	 **6**	10%[d, e]
	 **7a** 2-endo-3-exo **7b** 2-exo-3-endo	85%[f]	 **8**	89%
	 **9a** erythro, **9b** threo	83%[f]	 **10a** (Z), **10b** (E)	80%[f]
	 **11a, 11b** (cis, trans)	92%[f]	 **12**	92%
 R = H, Me, *n*-Pr	 **13** R = H **15** R = Me **17** R = *n*-Pr	60% 63% 83%	 **14** R = H **16** R = Me **18** R = *n*-Pr	95% 92% 85%
 R = H	 **19**  **20**	77%[f]	 **21**  **22**	92%[f, g]
R = Me	 **23**	57%	 **24**	38%[g]

[a]Literature yields are in parenthesis.
[b]Yields from the iodo(phenylsulfonyl) precursor.
[c]Iodosulfone **3** was accompanied by 5% of the cis isomer (17).
[d]Yield of side product from thermal elimination of **5**. Elimination on alumina was not investigated.
[e]Tosyl iodide gave 67% addition plus 10% thermal elimination product (17).
[f]Combined yield of isomers.
[g]Elimination did not occur on neutral alumina; carried out using DABCO.

yields of single *vic*-iodosulfones having the trans configuration. 1-Methylcyclohexene gave only *trans*-1-iodo-1-methyl-2-(phenylsulfonyl)cyclohexane, having the anti-Markovnikov regiochemistry, consistent with free radical, rather than ionic addition. The same regiochemistry, previously observed for reaction of alkenes with iodine and sodium arylsulfonates, was rationalized as being due to the steric bulk of the sulfinate anion, favoring rearside attack on the intermediate three-membered ring iodonium intermediates at the less-hindered position (18). However, an ionic pathway for such iodosulfonation reactions appears unlikely, since we observe that reaction of benzenesulfinic acid with NIS in dichloromethane-d_2 at room temperature gives benzenesulfonyl iodide at a rate similar to that for iodosulfonation of alkenes. A radical pathway is further supported by our observation that methyl vinyl ketone and the corresponding alcohol (3-buten-2-ol) undergo iodosulfonylation with NIS – benzenesulfinic acid at similar rates. Additionally, Yus and coworkers (21) have shown that reaction of α,β-unsaturated carbonyl compounds with sodium *p*-toluenesulfinate and iodine gives α-iodo-β-sulfonyl adducts, as expected for free radical addition.

Iodosulfonylation of *E*-4-octene gave a mixture of *threo*- and *erythro*-4-iodo-5-phenylsulfonyl octanes (**9a**, **9b**). This result is of interest in light of a report by Skell and McNamara (14) on reaction of phenylsulfonyl iodide with *cis*- or *trans*-2-butene, both of which gave identical mixtures of *threo*- and *erythro*-iodosulfones. The latter apparently formed via a 3-phenylsulfonyl-2-butyl radical, which undergoes conformational exchange at a rate competitive with that for iodine abstraction from phenylsulfonyl iodide to give the iodosulfonation product. No isomerization of starting butenes was observed (as occurred for chlorosulfonation with sulfonyl chlorides) (22), since iodine abstraction occurs faster than reversion of the phenylsulfonyl-2-butyl radical to alkene.

The mixture of *erythro*- and *threo*-4-iodo-5-(phenylsulfonyl)octanes (**9a**, **9b**) was inseparable by TLC. Although ^{1}H NMR revealed the isomers to be present in 71:29 molar ratio, their spectra were too similar to distinguish them. However, dehydroiodination on neutral alumina (vide infra) gave *E*- and *Z*-4-(phenylsulfonyl)octenes (**10a**, **10b**) in 67:32 molar ratio. Providing that elimination occurs by an E2 process, the major E isomer **10a** derives from the *erythro*-iodosulfone (**9a**) while the Z isomer **10b** forms via the *threo*-iodosulfone (**9b**).

Iodosulfonation of norbornylene gave a mixture of 2-*endo*-iodo-3-*exo*-(phenylsulfonyl)norbornane (**7a**) and a second compound, tentatively identified as the 2-*exo*-iodo-3-*endo*-phenylsulfonyl isomer **7b** in approximately equimolar ratio. Formation of **7a** is consistent with the intermediacy of the 3-*exo*-(phenylsulfonyl)-2-norbornyl radical, which would be trapped by iodine transfer from benzenesulfonyl iodide to the endo face. In contrast, **7b** apparently forms via the 2,3-*exo*-iodonium intermediate resulting from iodonium (I^+) transfer from NIS to norbornylene, followed by endo attack by the benzenesulfinate ion. It thus appears that iodosulfone formation via iodonium intermediates may be expected in cases involving more nucleophilic alkenes such as norbornylene.

1,3-Cyclohexadiene gave a mixture of *cis*/*trans*-3-iodo-6-(phenylsulfonyl)cyclohexene (**11a**, **11b**) in approximately equimolar ratio, determined from the integrated intensities for the CHI and $CHSO_2Ph$ peaks in the ^{1}H NMR spectrum. Vicinal coupling for H_6 indicated the sulfonyl group to be pseudoequatorial for the major isomer and pseudoaxial for the minor one; however, since J_{vic} values for H_3 could not be determined; it was not possible to distinguish the two isomers by NMR.

Dehydroiodination of α-iodo-β-alkylsulfonyl or arylsulfonyl compounds has previously been carried out using pyridine in benzene under reflux (14), or triethylamine in various solvents at room temperature, or with heating (12, 17–21, 23). In the present work, it was found that flash chromatography of *trans*-1-iodo-2-(phenylsulfonyl)cyclohexane (**3**) on neutral alumina resulted in partial conversion to 1-(phenylsulfonyl)cyclohexene (**4**). This led to the observation that dehydroiodination could be carried out preparatively, simply by stirring neutral alumina slurries of the iodosulfones in dichloromethane at room temperature to yield the corresponding α,β-unsaturated sulfones, generally in very good to excellent yields (Table 1). This procedure avoids the use of amine bases that may be incompatible with some functional groups. However, dehydroiodination of the iodosulfone TMBDS ethers **19**, **21**, and **23** (vide infra) did not occur on alumina. In these cases, we found that the elimination could be carried out using 1,4-diazabicyclo[2.2.2]octane (DABCO).

We were also interested in application of the iodophenylsulfonation–dehydroiodination sequence to the synthesis of γ-oxygenated, α,β-unsaturated phenylsulfones by using allylic alcohols or their derivatives as substrates. Products derived from allylic alcohols could thus serve as precursors to phenylsulfonyl-substituted, α,β-unsaturated ketones, which are established heterodienes in Diels–Alder reactions (24), as well as other synthetic applications involving conjugate additions (25). γ-Alkoxy-α,β-unsaturated phenylsulfones are useful as substrates in [3+2] cycloadditions, via π-allyl palladium complexes, as a method for cyclopentenone annulation (26), and also in six-membered ring annulations by a conjugate addition–alkylation sequence (27).

Examples of the allylic alcohols used as substrates in the iodophenylsulfonation–elimination sequence are shown in Table 1. Treatment of allyl alcohol with benzensulfinic acid and NIS in dry dichloromethane overnight gave a 54% yield of iodophenylsulfone **13**. The NMR spectrum indicated a single regioisomer, resulting from addition of the phenylsulfonyl group to the less-substituted carbon, consistent with our results for other unsymmetrically substituted alkenes. Treatment of the iodophenylsulfone with neutral alumina gave a nearly quantitative yield of the γ-hydroxy-α,β-unsaturated sulfone **14**, the structure of which was confirmed by comparison of physical data with reported values for this compound prepared by either microwave- or ultrasound-assisted alkylation of sodium benzenesulfinate by Villemin and Aloum (28).

Similarly, treatment of 3-butene-2-ol with benzenesulfinic acid and NIS gave iodophenylsulfone **15** as a mixture of diastereomers. Again, a single regiochemistry of addition was observed. Elimination w ith alumina occurred smoothly to give the known (29) γ-hydroxy-α,β-unsaturated sulfone **16**. An isomeric vinyl sulfone, 3-(phenylsulfonyl)-3-buten-2-ol, was previously prepared by the addition of phenyl vinyl

sulfone to acetaldehyde. Oxidation gave 3-(benzenesulfonyl)-3-buten-2-one, which was shown to undergo hetero-Diels–Alder reactions with vinyl ethers in high yield at or below room temperature (24). It is anticipated that the ketone derived by oxidation of **16** would also be useful as a heterodiene. Similarly, (*E*)-1-(phenylsulfonyl)-hex-1-en-3-ol (**18**) (30) was prepared from 1-hexen-3-ol in good overall yield by regioselective iodosulfonation–elimination.

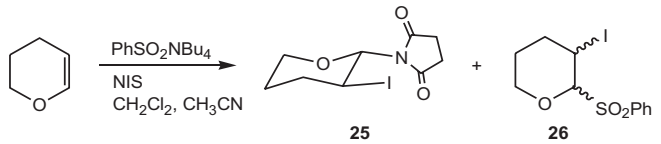
Both 2-cyclohexen-1-ol and 2-methyl-2-cyclohexen-1-ol were unsuitable as substrates for the synthesis of vinyl sulfones using the iodophenylsulfonation–elimination sequence because of side reactions. Better results were obtained using the *tert*-butyldimethylsilyl (TBDMS) ethers of these cyclic allylic alcohols. The attempted synthesis of 3-(*tert*-butyldimethylsiloxy)-1-(phenylsulfonyl)cyclohexene (**21**) from 2-cyclohexen-1-ol by this method resulted in a mixture of vinyl sulfones **21** and **22** because of a lack of regioselectivity in the initial addition step. Treatment of the TBDMS ether of 2-methyl-2-cyclohexen-1-ol gave diastereomeric 2-iodo-3-phenylsulfonyl derivatives (**23**), which were converted to vinyl sulfone **24**, albeit in lower overall yield than was observed for the other cases. Vinyl sulfone **21** was used in the synthesis of annulated cyclopentenones by Trost et al. (26).

Ley and co-workers (31) have developed synthetically useful alkylation reactions of anions derived from 2-benzensulfonyl tetrahydropyran. We decided to attempt the application of our iodophenylsulfonation reaction to dihydropyran and to glycals. The only products obtained from dihydropyran upon treatment with NIS – benzenesulfinic acid, were those resulting from addition of benzenesulfinic acid, suggesting that protonation of the double bond occurs faster than iodination, or alternatively, hydrogen atom abstraction by the adduct of DHP and benzenesulfonyl radical is again faster than iodination. We also attempted iodophenylsulfonation of dihydropyran using NIS and tetra-*N*-butylammonium benzenesulfinate and observed a significant amount of adduct **25** (apparently resulting from trapping of dihydropyran iodonium ion by succinimide), along with iodophenylsulfone **26** and other products that were not identified (Scheme 1).

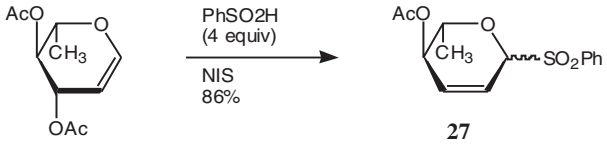
Iodophenylsulfonation of glycals was also attempted using NIS and benzenesulfinic acid in an effort to prepare carbohydrate vinyl sulfones. Ley and co-workers (31*a*) had observed that benzenesulfinic acid adds to tri-*O*-acetyl-L-glucal with double bond migration (Ferrier rearrangement). This same result was also observed in our study for the reaction of either tri-*O*-acetyl-D-glucal or di-*O*-acetyl-L-rhamnal, when treated with benzenesulfinic acid in the presence or absence of *N*-iodosuccinimide. In both cases, the Ferrier rearrangment product was obtained, with no evidence of iodophenylsulfone formation. Di-*O*-acetyl-L-rhamnal gave an 86% yield of the anomeric phenylsulfone adducts **27** when treated with excess benzenesulfinic acid at room temperature (Scheme 2).

In summary, a convenient two-step synthesis of α,β-unsaturated sulfones has been developed using iodophenylsulfonation of alkenes or alkenols with NIS – benzenesulfinic acid, followed by dehydroiodination on neutral alumina at room temperature. The overall process is highly regioselective for unsymmetrical alkenes, giving vinyl sulfones that can be used for a variety of synthetic applications.

Scheme 1.



Scheme 2.



Experimental

Preparation of benzenesulfinic acid

A stirred solution of sodium benzene sufinate (10.0 g, 61.0 mmol) in distilled water (25 mL) under nitrogen at 0 °C was slowly acidified to pH 1 by dropwise addition of 12 mol/L HCl. The white crystalline benzenesulfinic acid was filtered and air dried on a Büchner funnel, then stored at 0 °C (7.35 g, (85% yield); mp 82–86 °C (lit. value (32) mp 77 to 78 °C; (33) mp 82–84 °C).

General procedure for iodophenylsulfonation of alkenes using NIS – benzenesulfinic acid

To a stirred solution of NIS (225 mg, 1.0 mmol) in CH_2Cl_2 (50 mL) was added benzenesulfinic acid (142 mg, 1.0 mmol) and stirring continued for ~5 min to effect solution. The alkene (1.0 mmol) was added, and the reaction mixture was stirred for 30 min to 2 h at room temperature (monitored by TLC on silica gel using hexane – ethyl acetate, 1:1 *v*/*v* as eluent), then extracted with satd. aq. $NaHCO_3$ and $NaHSO_3$ (50 mL, each), dried ($MgSO_4$), and filtered. Flash chromatography on silica gel (60–200 mesh) using hexane – ethyl acetate (1:1) as eluent gave the oily liquid iodosulfones. No dehydroiodination products were detected, except in the case of iodosulfone **5**, which was accompanied by ~10% of 1-methyl-2-(phenylsulfonyl)cyclohexene (**6**).

trans-1-Iodo-2-(phenylsulfonyl)cyclopentane (1)

Yield: 322 mg (96%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.98 (m, 2H, Ph-H), 7.71 (m, 1H, Ph-H), 7.65 (m, 2H, Ph-H), 4.64 (ddd, 1H, H_1, $J_{1,2}$ = 4.2 Hz, $J_{1,5a}$ = 3.2 Hz, $J_{1,5b}$ = 3.0 Hz), 3.94 (ddd, 1H, H_2, $J_{1,2}$ = 4.2 Hz, $J_{2,3a}$ = 3.1 Hz, $J_{2,3b}$ = 3.0 Hz), 2.5–1.8 (cms, 6H, H_{3-5}) ^{13}C NMR (75.4 MHz, $CDCl_3$) δ: 138.8, 134.4, 129.8, 128.8 (Ph), 75.2 (C_2), 40.87 (C_5), 26.36, 25.41, 20.48 ($C_{1,3,4}$). The cyclopentane ring ^{1}H shifts are consistent with literature values for the corresponding 1-iodo-2-p-toluenesulfone (17).

trans-1-Iodo-2-(phenylsulfonyl)cyclohexane (3)

Yield: 238 mg (86%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.10–7.92 (m, 2H, Ph-H), 7.77–7.69 (m, 1H, Ph-H), 7.69–7.60 (m, 2H, Ph-H), 5.14 (bs, 1H, H_1), 3.41 (bs, 1H, H_2), 1.95–0.82 (cms, 8H, H_{3-6}). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ: 138.2 (C_i), 134.3 (C_p), 129.7 (C_o), 128.8 (C_m), 67.86 (C_2),

34.0 (C_6); 25.9, 23.6, 22.6, 21.5 (C_1, $C_{3–5}$). The ^{1}H NMR shifts are consistent with published data (17).

***trans*-1-Iodo-1-methyl-2-(phenylsulfonyl)cyclohexane (5)**

Yield: 328 mg (90%). IR (KBr, cm^{-1}) ν_{max}: 1300 (SO_2, ν_{asym}), 1130 (SO_2, ν_{sym}). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.92 (m, 2H, Ph-H), 7.64 (m, 1H, Ph-H), 7.55 (m, 1H, Ph-H), 3.70 (bs, 1H, H_2), 2.01 (s, 3H, CH_3), 2.2–1.1 (cms, 8H, $H_{3–6}$). The cyclohexyl ^{1}H shifts agree with those reported for *trans*-1-iodo-1-methyl-2-tosylcyclohexane (17). In addition to the iodosulfone **5**, column chromatography also gave 1-methyl-2-(phenylsulfonyl)cyclohexene (**6**, 24 mg, 10%) identified by comparison of the ^{1}H NMR spectrum with literature data (17).

2-Iodo-3-(phenylsulfonyl)norbornanes (7a, 7b)

Yield: 307 mg (85% combined yield; ~1:1 molar ratio by ^{1}H NMR). ^{1}H NMR (300 MHz, $CDCl_3$) for the 2-*endo*-iodo-3-*exo*-(phenylsulfonyl) isomer **7a** δ: 7.99 (m, 2H, Ph-H), 7.77 (m, 1H, Ph-H), 7.68 (m, 2H, Ph-H), 4.38 (cm, 1H, H_{2x}, $J_{2x,3n}$ = 5.9 Hz, $J_{1,2x}$= 3.7 Hz, $J_{2x,6x}$ = 1.7 Hz, $J_{2x,7s}$ = ~0 Hz; no COSY cross peak). A cross peak was observed for H_1-H_{2x}, aiding confirmation of H_{3n}, H_{2x}), 3.05 (dd, 1H, H_{3n}, $J_{2x,3n}$ = 5.9 Hz, $J_{3n,7a}$ = 1.7 Hz, $J_{3n,4}$ = ~0 Hz), 2.81 (m, 1H, H_4), 2.52 (m, 1H, H_1), 2.08 (m, 1H, H_{7s}), 1.67 (cms, 2H, H_{5x}, H_{6x}) 1.34 (m, 1H, H_{7a}), 1.27 (m,1H, H_{5n}), 1.08 (m, 1H, H_{6n}). ^{13}C NMR (75.4 MHz, $CDCl_3$) phenyl δ: 138.5 (C_i), 133.9 (C_p), 129.4 (C_m), 128.7 (C_o); norbornyl δ: 76.11 (C_3), 45.31 (C_1), 38.44 (C_4), 34.64 (C_7), 29.22 (C_5), 27.46 (C_6), 26.36 (C_1).

For 2-*exo*-iodo-3-*endo*-(phenylsulfonyl)norbornane (**7b**): ^{1}H NMR (300 MHz, $CDCl_3$) δ: 4.11 (dd, 1H, H_{2n}), 3.27 (dd, 1H, H_{3x}), 2.89 (bs, 1H, H_4), 2.50 (bs, 1H, H_1), 2.41 (d, 1H, H_{7s}), ~1.7–1.0 (ms, 5H, $H_{5,6}$, H_{7a}).

4-Iodo-5-(phenylsulfonyl)octane (9a, 9b)

Yield: 316 mg (83% combined yield); single component by TLC on silica gel (hexane – ethylacetate (1:1 *v*/*v* as eluent); however, ^{1}H NMR revealed the formation of **9a** and **9b** in 67:33 molar ratio. For the major isomer **9a**: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.88 (m, 2H, Ph-H), 7.62 (m, 1H, Ph-H), 7.59 (m, 2H, Ph-H), 4.61 (ddd, 1H, H_4, $J_{3a,4}$ = 10.8 Hz, $J_{3b,4}$ = 3.3 Hz, $J_{4,5}$ = 2.4 Hz), 3.54 (ddd, 1H, H_5, $J_{5,6a}$ = 7.7 Hz, $J_{5,6b}$ = 3.7 Hz, $J_{4,5}$ = 2.4 Hz), 2.11, 1.99 (ms, 2H, $H_{6a,6b}$), 1.77, 1.67 (ms, 2H, $H_{3a,3b}$), 1.41 (m, 2H, H_7), 1.55, 1.25 (ms, 2H, $H_{2a,2b}$), 0.91 (t, 3H, H_1, $J_{1,2}$ = 7.3 Hz), 0.88 (t, 3H, H_8, $J_{7,8}$ = 7.3 Hz); $J_{2,3}$ and $J_{6,7}$ were not determined. ^{13}C NMR (75.4 MHz, $CDCl_3$) δ: 139.3 (s, C_i), 134.4 (d, C_p), 129.8 (d, C_m) 128.7 (d, C_o), 72.53 (d, C_5), 36.52 (t, C_3), 31.84 (d, C_4), 28.21 (t, C_6), 23.89 (t, C_2), 22.46 (t, C_7), 14.18 (q, C_8), 13.23 (q, C_1). Anal. calcd. for $C_{14}H_{21}SO_2I$ (%): C 44.08, H 5.55, S 8.41; found (mixture of **9a** and **9b**): C 44.24, H 5.29, S 8.01.

For the minor isomer **9b**: ^{1}H NMR δ: 7.94 (m, 2H, Ph), 7.62 (m, 1H, Ph), 7.59 (m, 2H, Ph), 4.51 (ddd, 1H, H_4, $J_{3a,4}$ = 9.2 Hz, $J_{3b,4}$ = 5.4 Hz, $J_{4,5}$ = 2.2 Hz), 2.70 (ddd, 1H, H_5, $J_{5,6a}$ = 5.9 Hz, $J_{5,6b}$ = 5.2 Hz, $J_{4,5}$ = 2.2 Hz), 2.02, 1.73 (ms, 2H $H_{6a,6b}$), 1.99, 1.70 (ms, 2H, $H_{3a,3b}$), 1.43 (m, 2H, H_7), 1.50, 1.39 (ms, 2H, $H_{2a,2b}$), 0.88 (t, 3H, H_1, $J_{1,2}$ = 7.1 Hz), 0.875 (t, 3H, H_8, $J_{7,8}$ = 7.3 Hz). ^{1}H shifts for **9a** and **9b** were determined using COSY, HETCOR, and 1D decoupling; $J_{2,3}$ and $J_{6,7}$ were not determined. ^{13}C NMR (75.4 MHz, $CDCl_3$) for **9b** δ: 138.47 (s, C_i), 134.33 (d, C_p), 129.53 (d, C_m and C_o), 68.66 (d, C_5), 42.34 (t, C_3), 33.27 (t, C_6), 30.62 (d, C_4), 23.04 (t, C_2), 21.63 (t, C_7), 14.30 (q, C_8), 13.16 (q, C_1).

***cis*/*trans*-3-Iodo-6-(phenylsulfonyl)cyclohexene (11a, 11b)**

Yield: 319 mg (92% combined yield); single component by TLC on silica gel; ~1:1 molar ratio determined by ^{1}H NMR. Configurations at C_3 could not be assigned since vicinal couplings for H_3 were unobtainable owing to peak overlap. For **11a**: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.88 (m, 2H, Ph-H), 7.68 (m, 2H, Ph-H), 7.58 (m, 1H, Ph-H), 6.37 (dd, 1H, H_2, $J_{1,2}$ = 9.9 Hz, $J_{2,3}$ = 4.9 Hz), 5.61 (dd, 1H, H_1, $J_{1,2}$ = 9.9 Hz, $J_{1,6}$ = 4.4 Hz), 4.98 (m, 1H, H_3, $J_{2,3}$ = 4.9 Hz, $J_{3,6}$ = 1.0 Hz, $J_{1,3}$ = 1.0 Hz; $J_{3,4a}$ and $J_{3,4b}$ could not be determined), 3.95 (m, 1H, H_6, $J_{5,6a}$ = 5.6 Hz, $J_{5,6b}$ = 3.5 Hz, $J_{1,6}$ = 4.4 Hz, $J_{3,6}$ = 1.0 Hz), 2.17 (m, 2H, H_5), 2.08, 1.96 (ms, 2H, H_4). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ: 138.04 (C_2), 118.32 (C_1), 59.06 (C_6), 26.14 (C_4), 24.22 (C_3), 19.39 (C_5); Ph absorptions for **11a** and **11b**: 136.87, 135.72 (C_i), 128.92, 128.78 (C_m), 128.8, 128.42 (C_o), 133.71 (C_p, both isomers). For **11b**: ^{1}H NMR δ: 6.19 (dd, 1H, H_2, $J_{1,2}$ = 10.0 Hz, $J_{2,3}$ = 5.1 Hz), 5.84 (dd, 1H, H_1, $J_{1,2}$ = 10.0 Hz, $J_{1,6}$ = 2.6 Hz, $J_{1,3}$ = 1.3 Hz), 4.87 (m, 1H, H_3, $J_{2,3}$ = 5.1 Hz, $J_{3,6}$ = 1.8 Hz, $J_{1,3}$ = 1.3 Hz; $J_{3,4a}$ and $J_{3,4b}$ could not be determined), 4.22 (m, 1H, H_6, $J_{5,6a}$ = 10.7 Hz, $J_{5,6b}$ = 6.2 Hz, $J_{1,6}$ = 2.6 Hz, $J_{3,6}$ = 1.8 Hz), 2.11, 2.02 (ms, 2H, H_5), 2.11, 1.69 (ms, 2H, H_4). Ph absorptions overlapped those for **11a**. ^{13}C NMR (75.4 MHz, $CDCl_3$) δ: 136.81 (C_2), 119.30 (C_1), 61.65 (C_6), 30.96 (C_4), 23.68 (C_3), 20.00 (C_5). Anal. calcd. for $C_{12}H_{13}SO_2I$ (%): C 41.25, H 3.75, S 9.18; found for **11a** and **11b**: C 40.83, H 3.68, S 8.66.

A mixture of *cis*/*trans*-3-iodo-6-*p*-tosylcyclohexenes was previously obtained from reaction of 1,3-cyclohexadiene wth iodine/sodium *p*-toluenesulfinate (20).

General procedure for dehydroiodination of iodo(phenylsulfonyl) compounds 1, 3, 5, 7, 9, and 11

To a solution of the iodosulfonyl compound (1.0 mmol) in CH_2Cl_2 (50 mL) under nitrogen, neutral alumina (60–200 mesh, 100 cc) was added, and the resulting slurry was stirred for 1 day at rt, filtered, and the alumina was extracted with CH_2Cl_2 (50 mL). The combined extract was evaporated to give the crude α,β-unsaturated sulfone, which was purified by flash column chromatography on silica gel (toluene eluent, unless noted otherwise). Products were oily liquids, unless noted otherwise.

1-(Phenylsulfonyl)cyclopentene (2)

Flash chromatography on silica gel with hexane – ethyl acetate (1:1 *v*/*v*) as eluent (192 mg, 92%); mp 20–25 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.9 (m, 2H, Ph), 7.6 (m, 3H, Ph), 6.81 (dd, 1H, H_2, $J_{2,3a}$ = 3.8 Hz, $J_{2,3b}$ = 3.1 Hz) 3.1 (m, 4H, H_3, H_5), 2.1 (m, 2H, H_4); the ^{1}H shifts are consistent with literature (34) data. ^{13}C NMR (75.4 MHz, $CDCl_3$) phenyl δ: 140.1 (C_i), 133.65 (C_p), 129.46 (C_m), 128.21 (C_o); cyclopentenyl δ: 145.52, 140.51, 33.29, 31.19, 23.97.

1-(Phenylsulfonyl)cyclohexene (4)

Yield: 198 mg (95%); mp 39–43 °C. IR (KBr, cm^{-1}) ν_{max}: 1620 (C=C), 1300 (SO_2, ν_{asym}), 1140, (SO_2, ν_{sym}). ^1H NMR (300 MHz, $CDCl_3$) δ: 7.11 (dd, 1H, H_2, $J_{2,3a}$ = 4.3 Hz, $J_{2,3b}$ = 3.1 Hz), 2.35 (m, 2H, H_3, H_6), 1.8–1.5 (m, 4H, H_4, H_5); the shifts and splitting pattern for Ph were similar to those for **2**. The ^1H shifts are consistent with published (17, 34) values.

2-(Phenylsulfonyl)norbornene (8) (ref. 34)

Yield: 209 mg (89%). ^1H NMR (300 MHz, $CDCl_3$) δ: 6.93 (d, 1H, H_3, $J_{3,4}$ = 3.8 Hz), 3.14 (cm, 1H, H_1), 3.01 (cm, 1H, H_4), 1.79 (cm, 1H, $H_{6\text{-exo}}$), 1.67 (cm, 1H, $H_{5\text{-exo}}$), 1.52 (m, 1H, $H_{7\text{-syn}}$), 1.24 (m, 1H, $H_{7\text{-anti}}$), 1.10 (cm, 1H, $H_{6\text{-endo}}$), 0.96 (cm, 1H, $H_{5\text{-endo}}$); the Ph shifts and splitting patterns were similar to those for **7**. ^{13}C NMR (75.4 MHz, $CDCl_3$) phenyl δ: 140.22 (C_i), 133,59 (C_p), 129.50 (C_m), 128.09 (C_o); norbornenyl δ: 147.80 (C_2), 146.39 (C_3), 49.73 (C_7), 44.03 (C_4), 43.38 (C_1), 25.18 (C_5), 25.07 (C_6). Anal. calcd. for $C_{13}H_{14}SO_2$ (%): C 66.63, H 6.02, S 13.68; found: C 66.50, H 6.29, S 13.58.

(*Z*,*E*)-4-(Phenylsulfonyl)-4-octene (10a, 10b)

Flash chromatography (hexane – ethyl acetate, 1:1 *v*/*v*), 187 mg (80% combined yield); E:Z = 67:33 determined by ^1H NMR. For the Z isomer (**10a**): ^1H NMR (300 MHz, $CDCl_3$) δ: 7.884 (m, 2H, C_o), 7.60 (m, 1H, H_p), 7.53 (m, 2H, H_m), 6.008 (dd, 1H, H_5, $J_{5,6}$ = 7.9 Hz, $J_{3,5}$ = 1.2 Hz), 2.604 (m, 2H, H_6, $J_{5,6}$ = 7.9 Hz, $J_{6,7}$ = 7.4 Hz, $J_{3,6}$ = 1.2 Hz), 2.284 (ddd, 2H, H_3, $J_{2,3}$ = 7.5 Hz, $J_{3,5}$ = 1.2 Hz, $J_{3,6}$ = 1.2 Hz), 1.522 (m, 2H, H_2, $J_{2,3}$ = 7.5 Hz, $J_{1,2}$ = 7.4 Hz), 1.393 (m, 2H, H_7, $J_{6,7}$ = 7.4 Hz, $J_{7,8}$ = 7.4 Hz), 0.889 (t, 3H, H_8, $J_{7,8}$ = 7.4 Hz) 0.877 (t, 3H, H_1, $J_{1,2}$ = 7.4 Hz); the ^1H shifts are consistent with literature (35) data. ^{13}C NMR (75.4 MHz, $CDCl_3$) phenyl δ: 141.53 (s, C_i), 132.82 (d, C_p), 128.78 (d, C_m), 126.90 (d, C_o); octene chain δ: 142.99 (d, C_5), 140.20 (s, C_4), 34.80 (t, C_3), 30.21 (t, C_6), 22.19 (t, C_7), 22.10 (t, C_2), 13.39 (q, C_1), 13.11 (q, C_8). For the E isomer (**10b**): ^1H NMR δ: 7.857 (m, 2H, C_o), 7.60 (m, 1H, H_p), 7.53 (m, 2H, H_m), 6.927 (dd, 1H, H_5, $J_{5,6}$ = 7.5 Hz, $J_{3,5}$ = 0.5 Hz), 2.185 (m, 2H, H_6, $J_{5,6}$ = 7.5 Hz, $J_{6,7}$ = 7.5 Hz; $J_{3,6}$ could not be determined), 2.189 (m, 2H, H_3, $J_{2,3}$ = 6.5 Hz, $J_{3,5}$ = 0.5 Hz), 1.522 (m, 2H, H_7, $J_{6,7}$ = 7.5 Hz, $J_{7,8}$ = 7.5 Hz), 1.359 (m, 2H, H_2, $J_{1,2}$ = 7.5 Hz, $J_{2,3}$ = 6.5 Hz), 0.947 (t, 3H, H_8, $J_{7,8}$ = 7.5 Hz) 0.826 (t, 3H, H_1, $J_{1,2}$ = 7.5 Hz); the ^1H shifts agree with published (35) data. ^{13}C NMR phenyl δ: 140.83 (s, C_i), 132.79 (d, C_p), 128.80 (d, C_m), 127.65 (d, C_o); octene chain δ: 142.06 (d, C_5), 139.89 (s, C_4), 30.08 (t, C_3), 28.22 (t, C_6), 21.54 (t, C_7), 22.10 (t, C_2), 13.71 (q, C_1), 13.51 (q, C_8). The chemical shift and coupling assignments for **10a** and **10b** were made using a combination of correlated COSY, HETCOR, and 1-D decoupling. Anal. calcd. for $C_{14}H_{20}SO_2$ (%): C 66.33, H 7.99, S 12.71; found (**10a** and **10b**): C 65.92, H 7.81, S 12.35.

1-(Phenylsulfonyl)-1,3-cyclohexadiene (12) (refs. 3*a*, 34)

Yield: 203 mg (92%). ^1H NMR (300 MHz, $CDCl_3$) δ: 7.9 (m, 2H, Ph-H), 7.5 (m, 2H, Ph-H), 7.04 (dd, 1H, H_2, $J_{2,3}$ = 4.5 Hz, $J_{2,4}$ = 2.0 Hz), 7.61 (m, 1H, Ph-H), 6.11 (dd, 1H, H_3, $J_{3,4}$ = 9.4 Hz, $J_{2,3}$ = 4.5 Hz) Hz, 6.07 (cm, 1H, H_4) 2.35 (cm, 2H, H_6), and 2.27 (cm, 2H, H_5). ^{13}C NMR (75.4 MHz, $CDCl_3$) phenyl δ: 139.50 (C_i), 133.08 (C_p), 129.01 (C_m), 127.67 (C_o); cyclohexadiene δ: 136.05 (C_1), 133.21 (C_4),131.59 (C_2),122.5 (C_3), 22.9 (C_5), 19.9 (C_6). The ^1H shifts are similar to published (34) data.

General procedure for the synthesis of γ-oxygenated, α,β-unsaturated sulfones

Allylic alcohols or their *tert*-butyldimethylsilyl ethers were treated with 1 equiv. each of benzensulfinic acid and *N*-iodosuccinimide in anhydrous dichloromethane at room termperature. Progress of reactions was monitored by TLC using mixtures of ethyl acetate – hexanes as noted with each example shown in the following. The reaction mixture was diluted with dichloromethane (10 mL), then washed with 5% aqueous sodium thiosulfate solution, water, and brine, dried (sodium sulfate), and concentrated. Crude iodophenylsulfones were redissolved in dichloromethane and stirred overnight at room temperature with neutral alumina (10× excess by weight). The reaction mixture was filtered, solids were washed with ethyl acetate, and the filtrate was concentrated to give the vinyl sulfones that were purified further in some cases as noted. In the case of iodophenylsulfones **19**, **20**, and **23**, elimination was carried out by stirring overnight in carbon tetrachloride containing 1.3 equiv. of DABCO.

(*E*)-3-Phenylsulfonyl-2-propen-1-ol (14)

Allyl alcohol was converted to the iodophenylsulfonyl derivative **13** in 60% yield as described in the previous paragraph. R_f 0.17 (40% ethyl acetate – hexanes). IR (ATR, cm^{-1}) ν_{max}: 3495 (OH), 3064, 2934, 1447, 1300 (S=O), 1142 (S=O), 1082. ^1H NMR ($CDCl_3$) δ: 7.9 (m, 2H, PhH), 7.7 (m, 3H, PhH), 4.57 (sextet, 1H, *J* = 4.5 Hz, CHI), 4.04 (dd, 1H, *J* = 4.5, 12.6 Hz, CHOH), 3.93 (dd, 1H, *J* = 4.5, 12.6 Hz, CHOH), 3.93 (dd, 1H, *J* = 9.6 Hz, $PhSO_2CH_2$), 3.67 (dd, 1H, *J* = 4.5 Hz, $PhSO_2CH_2$), 2.43 (bs, 1H, OH). ^{13}C NMR ($CDCl_3$) δ: 139.0, 134.6, 129.8, 128.2, 67.4 (CHOH), 62.3 (CH_2SO_2Ph), 22.0 (CHI). HRMS calcd. for $C_9H_{12}O_3SI$: 325.9552 (M + H); found: 325.9561.

Elimination as described in the general procedure gave crystalline vinyl sulfone **14** (202 mg, 95%); mp 134–136 °C (lit. value (27) mp 139 to 140 °C). R_f 0.18 (ethyl acetate – hexanes, 1:1). ^1H NMR ($CDCl_3$) δ: 7.9 (m, 2H, PhH), 7.6 (m, 3H, PhH), 7.06 (m, 1H, *J* = 18 Hz, C=CH), 6.66 (m, 1H, *J* = 18 Hz, C=CH), 4.42 (m, 2H, CH_2OH), 1.6, (bs, 1H, OH). The ^1H NMR spectrum of **14** reported in the literature lists the vinylic hydrogens as a multiplet at δ 7.1–6.6, the CH_2OH methylene hydrogens as a multiplet at δ 5.55–4.20, and the hydroxyl proton resonance as a broad singlet at δ 3.90 (28).

(*E*)-4-Phenylsulfonyl-3-buten-2-ol (16)

3-Butene-2-ol (72 mg, 1 mmol) was converted to diastereomeric 3-iodo-4-phenylsulfonyl-2-butanols (**15**). Yield: 216 mg (63%). R_f 0.23 (40% ethyl acetate – hexanes). IR (ATR, cm^{-1}) ν_{max}: 3531 (OH), 2960, 1447, 1280 (S=O), 1142 (S=O), 1082. ^1H NMR δ: 7.90 (m, 2H, PhH), 7.62 (m, 3H, PhH), 4.60 (ddd, 1H, *J* = 9.8, 4.2, 2.0 Hz, CHI), 4.53 (td, 1H, *J* = 6.6, 4.2 Hz, CHI), 4.06 (dd, 1H, *J* = 14.2, 9.8 Hz, $PhSO_2CH$), 3.74 (d, 2H, *J* = 6.6 Hz, $PhSO_2CH_2$), 3.70 (dd, 1H, *J* = 14.2, 4.4 Hz, $PhSO_2CH$), 3.62, (bs or dq if OH is decoupled, 1H, *J* = 4.2, 6.1 Hz, CHOH), 3.43 (bs or dq if OH is decoupled, 1H, *J* = 5.9, 2.0 Hz, CHOH), 2.20

(bs, OH), 1.29 (d, 3H, J = 6.1 Hz, CH_3), 1.27 (d, 3H, J = 5.9 Hz, CH_3). ^{13}C NMR ($CDCl_3$) δ: 134.1, 134.0, 128.4, 128.4, 128.0, 127.7, 69.7 (CHOH), 67.7 (CHOH), 62.5 ($PhSO_2CH_2$), 62.0 ($PhSO_2CH_2$), 32.6 (CHI), 30.7 (CHI), 25.0 (CH_3), 20.9 (CH_3). HRMS calcd. for $C_{10}H_{14}O_3SI$: 340.9708 (M + H); found: 340.9705.

Treatment with alumina (2.1 g) gave 122 mg (92%) of vinyl sulfone **16**; mp 74 to 75 °C (lit. value (29) mp 64–66 °C. R_f 0.19 (40% ethyl acetate – hexanes). The ^{1}H NMR spectrum of **16** matched that reported (29).

(*E*)-1-(Phenylsulfonyl)hex-1-en-3-ol (18)

1-Hexen-3-ol (100 mg, 1 mmol) was converted to diastereomeric 2-iodo-1-(phenylsulfonyl)hex-1-en-3-ols (**17**). Yield: 305 mg (83%). R_f 0.36 (40% ethyl acetate – hexanes). IR (ATR, cm^{-1}) ν_{max}: 3497, 2959, 2933, 1447, 1304 (S=O), 1142 (S=O) 1083. ^{1}H NMR δ: 7.90 (m, 2H, PhH), 7.60 (m, 3H, PhH), 4.62 (ddd, 1H, J = 10.0, 4.3, 2.0 Hz, CHI), 4.49 (td, 1H, J = 6.9, 6.3, 4.1 Hz, CHI), 4.09 (dd, 1H, J = 14.2, 10.0 Hz, $PhSO_2CH$), 3.79 (dd, 1H, J = 15.4, 6.3 Hz, $PhSO_2CH_2$), 3.71 (dd, 1, J = 15.4, 6.9 Hz, $PhSO_2CH$), 3.70 (dd, 1, J = 14.2, 4.3 Hz, $PhSO_2CH$), 3.54 (cm, 1H, J = 4.1 Hz, CHOH), 3.11 (cm, 1H, J = 2.0 Hz, CHOH), 2.10 (bs, OH), 1.64–1.32 (m, 2 × 4H, CH_2), 0.96 (m, 3H, J = 6.9 Hz, CH_3), 0.94 (m, 3H, J = 6.7 Hz, CH_3). ^{13}C NMR ($CDCl_3$) δ: 138.7, 138.5, 134.0, 134.0, 129.4, 129.3, 129.3, 128.0, 127.7, 74.3 (CHOH), 71.0 (CHOH), 62.6 ($PhSO_2CH_2$), 61.5 ($PhSO_2CH_2$), 41.3, 36.5, 31.6, 28.6, 18.7, 18.5, 13.9, 13.9. HRMS calcd. for $C_{12}H_{18}O_3SI$: 369.0021 (M + H); found: 369.0021.

Treatment with alumina (3 g) gave 211 mg (88%) of vinyl sulfone **18**; mp 54–57 °C (lit. value (30) mp 56–58 °C). R_f 0.25 (40% ethyl acetate – hexanes). The ^{1}H and ^{13}C NMR spectra of **18** matched those reported (30).

3-(*tert*-Butyldimethylsiloxy)-1-(phenylsulfonyl)cyclohexene (21) and 3-(*tert*-butyldimethylsiloxy)-2-(phenylsulfonyl)cyclohexene (22)

Iodophenylsulfonation of the TBDMS ether of cyclohexenol gave a mixture of regioisomeric 2-iodo-1-phenylsulfonyl and 1-iodo-2-phenylsulfonyl derivatives (**19**, **20**); from 214 mg (1 mmol) of alkene there was obtained 371 mg (77%) of iodophenylsulfonyl adducts as an oil. R_f 0.36 (10% ethyl acetate – hexanes). ^{1}H NMR δ: 7.90 (m, 2H, PhH), 7.60 (m, 3H, PhH), 5.15 (m, 1H), 4.90 (m, 1H), 4.40 (m, 1H), 3.61 (m, 1H), 3.51 (m, 1H), 3.19 (m, 1H), 2.14–1.90 (m, 4H), 1.66–1.48 (m, 2H), 0.90 (s, *t*-Bu), 0.82 (s, *t*-Bu), 0.06 (s, CH_3), 0.04 (s, CH_3).

The crude mixture was taken up in carbon tetrachloride (3 mL), DABCO was added (112 mg, 1.3 equiv.), and the mixture was stirred overnight at room temperature. The mixture was diluted with dichloromethane, extracted with water and brine, dried (Na_2SO_4), and concentrated to give 262 mg (92%) of a mixture of vinyl sulfone **21** and its regioisomer **22**, which were not separated. R_f 0.27 (10% ethyl acetate – hexanes). The ^{1}H NMR spectrum of the mixture of vinyl sulfones showed a 2.2:1 ratio of vinyl sulfone **21** (the resonances of which matched those reported in the literature, ref. 27) and another product, assigned as the regioisomeric vinyl sulfone **22**, which showed peaks at δ 7.17 (C=CH) and 4.66 (CHOSi). HRMS calcd. for $C_{18}H_{29}O_3SiS$: 353.1607 (M + H); found: 353.1612.

3-(*tert*-Butyldimethylsiloxy)-2-methyl-1-(phenylsulfonyl)-cyclohexene (24)

The TBDMS ether of 2-methylcyclohexenol gave diastereomeric 2-iodo-3-phenylsulfonyl derivatives (**23**) and a small amount of a side product that was not identified; from 266 mg (1.18 mmol) of alkene there was obtained 334 mg (57%) of iodophenylsulfonyl adducts as an oil. R_f 0.30 (10% ethyl acetate – hexanes). ^{1}H NMR δ: 7.89 (m, 2H, PhH), 7.51 (m, 3H, PhH), 3.83 (m, 1H), 3.12 (m, 1H), 2.75 (m, 1H), 2.47–1.41 (m, 6H), 1.29 (s, 3H, CH_3), 1.26 (s, 3H, CH_3), 0.85 (s, *t*-Bu), 0.83 (s, *t*-Bu), 0.06 (s, CH_3), 0.04 (s, CH_3).

The crude mixture was taken up in carbon tetrachloride (3 mL), DABCO was added (88 mg, 1.3 equiv.), and the mixture was stirred overnight at room temperature. The mixture was diluted with dichloromethane, extracted with water and brine, dried (Na_2SO_4), and concentrated to give 196 mg of a mixture of products that was purified using a Waters vacuum manifold with a 20 Sep-Pak silica gel cartridge and 5%–20% ethyl acetate – hexanes as eluant to give 95 mg (38%) of vinyl sulfone **24** as an oil. R_f 028 (10% ethyl acetate – hexanes). ^{1}H NMR δ: 7.86 (m, 2H, PhH), 7.60 (m, 3H, PhH), 3.87 (m, 1H, CHOSi), 3.12 (m, 1H), 2.45 (s, 3H, CH_3), 2.36–1.24 (m, 6H), 1.29 (s, CH_3), 0.93 (s, *t*-Bu), 0.13 (s, CH_3), 0.12 (s, CH_3). HRMS calcd. for $C_{19}H_{31}O_3SiS$: 366.1763 (M + H); found: 366.1772

Phenylsulfonyl 4-*O*-acetyl-2,3,6-trideoxy-α,β-L-*threo*-hex-2-enopyranoside (27)

Benzenesulfinic acid (560 mg, 4 equiv.) was added to a stirring solution of 3,4-di-*O*-acetyl-6-deoxy-L-glucal (214 mg, 1 mmol) in 5 mL of anhydrous dichloromethane at 0 °C. The reaction was allowed to warm to room temperature and stirred for 1 h, after which TLC (20% ethyl acetate – hexane) showed that starting material was consumed. The mixture was then diluted with 40 mL of dichloromethane and washed with 10% $NaHCO_3$ (40 mL) and brine (40 mL), dried (Na_2SO_4), and concentrated to an oil that was purified on a Waters vacuum manifold using a 20 cc Sep-Pak silica gel cartridge and 20% ethyl acetate – hexane as eluant to give a 3:1 mixture of α and β anomers that were not separated. Yield: 255 mg (86%). R_f 0.4 (40% ethyl acetate – hexanes). ^{1}H NMR (300 MHz, $CDCl_3$): see Table 2. ^{13}C NMR (75.4 MHz, $CDCl_3$) δ: 169.8, 169.4, 136.6, 134.0, 133.7 (C_2/C_3), 132.9 (C_2/C_3), 129.6, 128.7, 128.6, 128.1, 120.9 (C_2/C_3), 119.0 (C_2/C_3), 89.3 (C_1, α), 88.1 (C_1, β), 72.4, 68.7, 68.4, 20.7, 20.6, 17.8, 17.5. Analytical MW calcd. for $C_{14}H_{16}O_5S$: 296; found by ESIMS: 314.3 (38%) $(M + NH_4)^+$, 155.3 (100%). HRMS calcd. for $C_{14}H_{17}O_5S$: 296.0797 (M + H); found: 297.0787.

Iodophenylsulfonation of dihydropyran

Dihydropyran (252 mg, 3 mmol) was dissolved in a mixture of 3 mL each of anhydrous acetonitrile and anhydrous dichloromethane. Tetra-*N*-butylammonium benzenesulfinate (36) (3 mmol, 1.15 g) and 4 Å molecular sieves (100 mg) were added and the reaction mixture was stirred for 30 min, then *N*-iodosuccinimide (675 mg, 3 mmol) was added and

Table 2.

	α Anomer	β Anomer
δ_H, J	δ_H	δ_H
H_1	5.075	5.226
H_2	6.234	5.943[a,b]
H_3	6.234	6.120[a]
H_4	5.017	4.520
H_5	4.390	3.588
H_6	1.196	1.220
OAc	2.092	2.031
H_o	7.937	7.879
H_m	7.594	7.544
H_p	7.702[c]	7.693
$J_{1,2}$	[d]	2.1
$J_{1,3}$	[d]	2.2
$J_{1,4}$	2.5	2.7
$J_{1,5}$	0.7	~0
$J_{2,3}$	~10.5	10.5
$J_{2,4}$	[d]	1.7
$J_{3,4}$	[d]	2.2
$J_{4,5}$	8.4	8.4
$J_{5,6}$	6.3	6.1

[a]H_2 and H_3 shifts, including related coupling constants, may need to be exchanged.
[b]Broadened dt multiplet.
[c]Shifts determined with the help of COSY.
[d]The coupling constants could not be determined because of the small $\Delta\delta$ between H_2 and H_3, generating high order multiplets.

the reaction was allowed to stir for 8 h at –78 °C. The reaction was diluted with dichloromethane (50 mL), washed with 10% $NaHSO_3$ (50 mL), water (50 mL), and brine (50 mL), dried over Na_2SO_4, and concentrated to give a yellow oily product that was then purified by flash chromatography over silica gel using 40% ethyl acetate in hexanes as the eluant. One of the products separated as a waxy solid (101 mg, 11%) was determined to be the *trans*-3-iodo-2-succinimide adduct of dihydropyran. The other fractions contained a mixture (211 mg) of the 3-iodo-2-phenylsulfonyl adducts and other side products that were not identified. The *trans*-3-iodo-2-succinimide **26** adduct had: R_f 0.28 (40% ethyl acetate – hexane). IR (film, cm^{-1}) ν_{max}: 2950, 1716, 1371. ^1H NMR δ: 5.24 (d, 1H, J = 11.2 Hz, CHN), 5.16 (ddd, 1H, J = 2.8, 11.2 Hz, CHI), 4.15 (m, 1H), 3.68 (m, 1H), 2.74 (s, 4H, CH_2CH_2), 2.60 (m, 1H), 2.13 (m, 1H), 1.78 (m, 1H), 1.40 (m, 1H). ^{13}C NMR δ: 178.2, 86.2, 71.6, 39.9, 31.2, 30.4, 26.7. HRMS calcd. for $C_9H_{13}NO_3I$: 309.9940; found: 309.9942.

The 3-iodo-2-phenylsulfonyl adducts **27** had: R_f 0.5 (40% ethyl acetate – hexane). IR (film, (cm^{-1}) ν_{max}: 2950, 1625, 1439, 1320 (S=O), 1139 (S=O). ^1H NMR δ: 5.01 (d, 1H, J = 5.6 Hz, CHS) 4.86 (d, 1H, J = 6.7 Hz, CHS), 4.21–3.98 (m, 2H), 3.72 (m, 1H), 3.62 (m, 1H), 2.2–1.6 (m, 10H). HRMS calcd. for $C_{11}H_{12}O_3SI$: 350.9548 (M – H); found: 350.9582.

Acknowledgments

The authors thank Dr. John Wojcik for conducting experiments that revealed the formation of benzenesulfonyl iodide from benzenesulfinic acid and *N*-iodosuccinimide. We also thank Villanova University for financial support of this research.

References

1. Reviews: (*a*) T. Durst. *In* Comprehensive organic chemistry. Vol. 3. *Edited by* D.N. Jones. Pergamon Press, Oxford. 1979. p. 171; (*b*) M.P. Bertrand. Org. Prep. Proced. Int. **26**, 257 (1994); (*c*) C. Chatgilialoglu, M.P. Bertrand, and C. Ferreri. *In* S-Centered radicals. *Edited by* Z.B. Alfassi. John Wiley, New York. 1999. Chap. 11.
2. (*a*) M. Asscher and D. Vofsi. J. Chem. Soc. 4962 (1964); (*b*) A. Orochov, M. Asscher, and D. Vofsi. J. Chem. Soc. (B), 255 (1969); (*c*) J. Sinnreich and M. Asscher. J. Chem. Soc. Perkin Trans. 1, 1543 (1972).
3. (*a*) W.E. Truce, C.T. Goralski, L.W. Christensen, and R.H. Bavry. J. Org. Chem. **35**, 4217 (1970); (*b*) W.E. Truce and C.T. Goralski. J. Org. Chem. **35**, 4220, (1970); (*c*) W.E. Truce and C.T. Goralski. J. Org. Chem. **36**, 2536 (1971).
4. J.-P. Pillot, J. Dunoguès, and R. Calas. Synthesis, 469 (1977).
5. I. De Riggi, J.-M. Surzur, and M.P. Bertrand. Tetrahedron, **44**, 7119 (1988).
6. (*a*) N. Kamigata, H. Sawada, and M. Kobayashi. J. Org. Chem. **48**, 3793 (1983); (*b*) N. Kamigata, J. Ozaki, and M. Kobayashi. J. Org. Chem. **50**, 5045 (1985); (*c*) N. Kamigata, K. Udodaira, and T. Shimizu. J. Chem Soc. Perkin Trans. 1, 783 (1997).
7. M.S. Kharasch and A.F. Zavist. J. Am. Chem. Soc. **73**, 964 (1951).
8. (*a*) S.J. Cristol and J.A. Reeder. J. Org. Chem. **26**, 2182 (1961); (*b*) S.J. Cristol and D.I. Davies. J. Org. Chem. **29**, 1282 (1964).
9. W. Böll. Liebigs Ann. Chem. 1665 (1979).
10. H. Goldwhite, J.S. Gibson, and C. Harris. Tetrahedron, **21**, 2743 (1965).
11. A.S. Gozdz and P. Maslak. J. Org. Chem. **56**, 2179 (1991).
12. C.M.M. da Silva Corrêa and W.A. Waters. J. Chem. Soc. (C), 1874 (1968).
13. Y. Takahara, M. Iino, and M. Matsuda. Bull. Chem. Soc. Jpn. **49**, 2268 (1976).
14. P.S. Skell and J.H. McNamara. J. Am. Chem. Soc. **79**, 85 (1957).
15. W.E. Truce, D.L. Heuring, and G.C. Wolf. J. Org. Chem. **39**, 238 (1974).
16. C.M.M. da Silva Corrêa, M.D.C.M. Fleming, M.A.B.C.S. Oliveira, and E.M.J. Garrido. J. Chem. Soc. Perkin Trans 2, 1993 (1994).
17. L.K. Liu, Y. Chi, and K.-Y. Jen. J. Org. Chem. **45**, 406 (1980).
18. L.M. Harwood, M. Julia, and G. Le Thuillier. Tetrahedron, **36**, 2487 (1980).
19. (*a*) K. Inomata, T. Kobayashi, S.-i. Sasaoka, H. Kinoshita, and H. Kotake. Chem. Lett. 289 (1986); (*b*) K. Inomata, S-i. Sasaoka, T. Kobayashi, Y. Tanaka, S. Igarashi, T. Ohtani, H. Kinoshita, and H. Kotake. Bull. Chem. Soc. Jpn. **60**, 1767 (1987).
20. J. Barluenga, J.M. Martinez-Gallo, C. Nájera, F.J. Fañanás, and M. Yus. J. Chem. Soc. Perkin Trans. 1, 2605 (1987).
21. C. Nájera, B Baldó, and M. Yus. J. Chem. Soc. Perkin Trans. 1, 1029 (1988).
22. P.S. Skell, R.C. Woodworth, and J.H. McNamara. J. Am. Chem. Soc. **79**, 1253 (1957).
23. Synthesis of vinyl sulfones via iodosulfone intermediates has

also been carried out by Ce(IV)-mediated reaction of alkenes with aryl sulfinates and sodium iodide: V. Nair, A. Augustine, and T.D. Suja. Synthesis, 2259 (2002).
24. A. Weichert and H.M.R. Hoffmann. J. Org. Chem. **56**, 4098 (1991).
25. N.S. Simpkins. Sulphones in organic synthesis. Tetrahedron organic series Vol. 10. Pergamon Press, New York. 1993.
26. B.M. Trost, P. Seoane, S. Mignani, and M. Acemoglu. J. Am. Chem. Soc. **111**, 7487 (1989).
27. J. Ponton and P. Helquist. J. Org. Chem. **46**, 118 (1981).
28. D. Villemin and A.V. Aloum. Synth. Commun. **20**, 925 (1990).
29. E. Dominguez and J.C. Carretero. Tetrahedron, **46**, 7197 (1990).
30. A.D Westwell, M. Thornton-Pett, and C.M. Rayner. J. Chem. Soc. Perkin Trans. 1, 847 (1995).
31. (*a*) D.S. Brown, M. Bruno, R.J. Davenport, and S.V. Ley. Tetrahedron, **45**, 4293 (1989); (*b*) S.V. Ley, S.F. Lygo, and A. Wonnacott. Tetrahedron, **42**, 4333 (1986).
32. M. Uchino, K. Suzuki, and M. Sekiya. Chem. Pharm. Bull. **26**, 1837 (1978).
33. H.J. Shine, M. Rahman, H. Seeger, and G.-S. Wu. J. Org. Chem. **32**, 1901 (1967).
34. P.B. Hopkins and P.L. Fuchs. J. Org. Chem. **43**, 1208 (1978).
35. L. Benati, L. Capella, P.C. Montevecchi, and P. Spagnolo. J. Chem. Soc. Perkin Trans. 1, 1035 (1995).
36. G.E. Vennstra and B. Zwaneburg. Synthesis, 519 (1975).