Free Radical Self-Immolative 1,2-Elimination and Reductive Desulfonylation of Aryl Sulfones Promoted by Intramolecular Reactions with *Ortho*-Attached Carbon-Centered Radicals[1]

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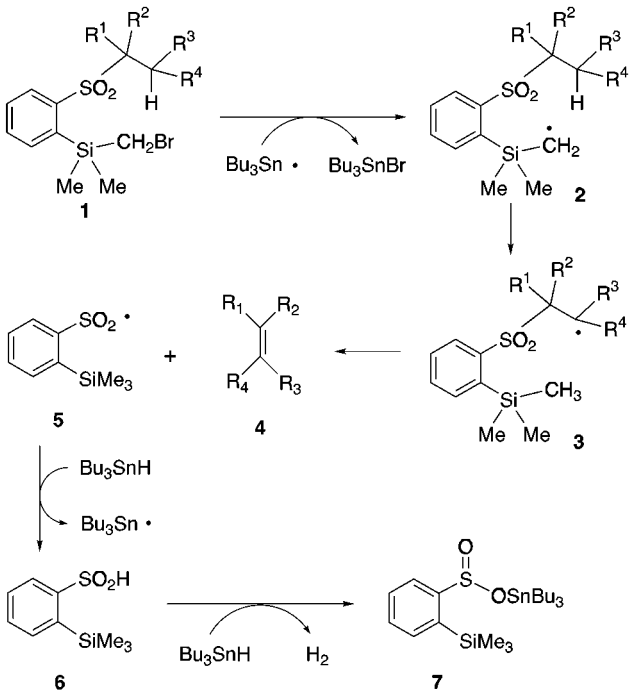
Aryl sulfones bearing an *o*-(bromomethyl)dimethylsilyl moiety (**1**), when heated with AIBN and tributyltin hydride, suffer radical elimination under mild conditions to give olefins and stannyl sulfinate **7** in high yield. The mechanism is shown to proceed via intramolecular β-sulfonyl hydrogen abstraction by *o*-silylmethylene radical **2**. This step also shows a large deuterium isotope effect of 12:1. In contrast, radical intermediate **24**, generated by tris(trimethylsilyl)silane radical addition to *o*-allylsilane **23**, undergoes intramolecular attack on the sulfone, resulting in homolytic sulfone cleavage to afford reduced products and cyclic sulfone byproduct **25**.

Introduction

Familiar synthetic applications which rely on the inductive effect of the aryl sulfone functional group include conjugate addition to vinyl sulfones and alkylation reactions of α-sulfonyl anions. Aggressive strategies which seek further functionalization can be seen to exploit the sulfone as a leaving group.[2] Olefin-forming reactions involving sulfinic acid elimination of aryl sulfones are generally promoted by α-heteroatom substitution[3] or by allylic (π) activation of protons β to the sulfone.[4] In absence of activation, simple alkyl aryl sulfones require treatment with strong base at high temperature to afford olefin products via sulfinic acid elimination.[5] In addition, although radical mediated elimination has been demonstrated for β-bromo and β-nitro aryl sulfones,[6] to our knowledge, there are no examples of aryl sulfones lacking β-activation which eliminate to olefins under standard AIBN/tributyltin hydride free radical conditions.

We have been investigating *ortho*-substitution of aryl sulfones as a means of generating activated intermediates to facilitate sulfone cleavage. It was previously reported that *o*-(allyldimethylsilyl)aryl sulfones, when converted to the silyl triflate moiety, undergo intramolecular oxygen silylation forming silyl sultinium intermediates which eliminate under mild conditions to afford olefins.[7] In a recent study,[8] the *ortho*-activation strategy was utilized to promote homolytic cleavage of allylic sulfones via intramolecular attack of *o*-stannyl radicals on the sulfonyl group.

Scheme 1



Results and Discussion

In our efforts to generate *ortho*-radical species capable of activating nonallylic tertiary sulfones toward homolytic cleavage, we examined *o*-(bromomethyl)silyl species **1** (Scheme 1). It was found that silylmethylene radical **2** (generated by heating **1** along with AIBN and slow addition of tributyltin hydride, or by irradiating **1** in the presence of bis(tributyltin)) does not attack the sulfonyl group but instead abstracts a hydrogen β to the sulfone via an unusual 8-membered ring transition state to produce β-sulfonyl radical **3**. The concentration of tributyltin hydride must be kept low to minimize its quenching of silylmethylene radical **2**. Intermediate **3** rapidly suffers sulfonyl radical elimination to afford olefin **4** and arylsulfonyl radical **5**. Radical **5** is quenched with tributyltin hydride, propagating the radical chain reaction with concomitant generation of sulfinic acid **6**. A

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Table 1. Conditions and Yields for Radical-Mediated Sulfone Elimination Reaction

Entry #	; R =	Method[a]	Major Product	NMR Yield
1	Ph–C≡C– **8a**	a	Ph–C≡C–	88 %[b]
2	**8b**	b		88 %
3	**8c**	b		46 %
4	**8d**	b		85 %[c]

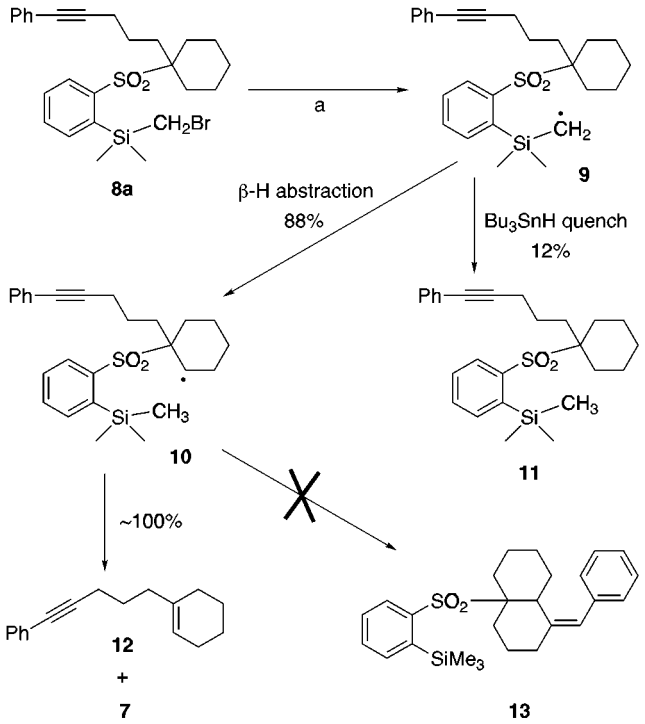
[a] Method a: 1,3,5-trimethoxybenzene (NMR internal standard, 0.3 equiv), AIBN (0.3 equiv), slow addition of Bu_3SnH (2.0 equiv) over ~10 h, C_6D_6, 80 °C, 13 h. Method b: 1,3,5-trimethoxybenzene (NMR internal standard, 0.3 equiv), $(Bu_3Sn)_2$ (1.5 equiv), *hν* (350 nm), C_6D_6, 18 h. [b] A 63% unoptimized isolated yield was obtained. [c] Yield based on stannyl sulfinate byproduct due to volatility of olefin product.

second molecule of tributyltin hydride then reacts with **6** to produce stannyl sulfinate **7** as the observed byproduct along with molecular hydrogen. Two equivalents of tributyltin hydride are therefore required to complete the reaction. This is consistent with previous observations[9] that arylsulfonyl radicals, generated in the presence of tributyltin hydride, consumed a second equivalent of tributyltin hydride to form stannyl sulfinate derivatives. When bis(tributyltin) is used, a reaction between arylsulfonyl radical **5** and bis(tributyltin) propagates the radical chain producing **7** and a tributylstannyl radical. Stannyl sulfinate **7** is unstable on silica gel and was not isolated. However, it is clearly visible by ^1H NMR during NMR tube reactions, and mass spectra of the crude reaction mixture display a strong and distinctive molecular ion corresponding to **7**. Table 1 shows products and yields obtained from radical-mediated elimination of unactivated tertiary *o*-[(bromomethyl)silyl]aryl sulfones. It is believed that the low yield observed for entry 3 of Table 1 is due to a competing pathway where the *o*-silylmethylene radical abstracts a benzylic hydrogen from the carbon γ to the sulfone, generating a benzylic radical which is incapable of β-elimination.

Ortho-attachment of the (bromomethyl)dimethylsilyl moiety was readily accomplished via directed metalation[10] of phenyl sulfones bearing no acidic α-protons followed by treatment with (bromomethyl)chlorodimethylsilane to afford *o*-[(bromomethyl)dimethylsilyl]aryl sulfones **8a**−**d** in 81−87% yield.

An NMR study of the radical-mediated sulfone elimination reaction was carried out using *o*-[(bromomethyl)dimethylsilyl]aryl sulfone **8a** as the starting material (Scheme 2). The major portion of silylmethylene radical intermediate **9** suffered intramolecular β-sulfonyl hydrogen abstraction to form β-sulfonyl radical intermediate **10** which fragmented to afford eneyne **12** in 88% NMR yield (63% unoptimized isolated yield). The remaining

Scheme 2[a]



[a] Reagents and conditions: (a) AIBN (0.5 equiv), Bu_3SnH (2.2 equiv, added over 14 h), C_6D_6, 80 °C, 15 h.

portion of intermediate **9** was quenched by tributyltin hydride before β-hydrogen abstraction could take place, thereby affording reduced trimethylsilyl product **11** in 12% NMR yield.

Although there are reports of β-sulfonyl radicals undergoing intramolecular cyclizations with electron deficient olefins,[11] intermediate **10**, which contains a good radical acceptor with favorable regiochemistry, does not produce cyclized product **13** in observable quantities. This suggests that once formed, β-sulfonyl radical intermediate **10** is short-lived and that the rate-determining step for the overall reaction is the β-sulfonyl hydrogen abstraction step.

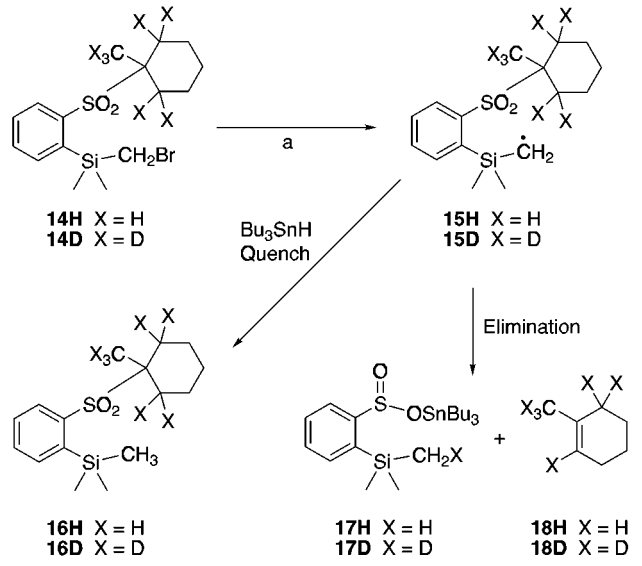
In preparation for a double-labeling study to determine whether β-hydrogen abstraction is strictly intramolecular, compound **14D** with all β-sulfonyl hydrogens replaced by deuterium was synthesized. In preliminary experiments with **14D**, a surprisingly large primary deuterium isotope effect was observed for the β-sulfonyl hydrogen abstraction step. To quantitatively determine the isotope effect, compound **14D** and its completely protonated analog **14H** were heated with AIBN and tributyltin hydride under identical conditions (Scheme 3). A mixture of tributyltin hydride quenched products **16** and elimination products **17** and **18** were produced in both reactions. The rate at which intermediates **15H** and **15D** are quenched with tributyltin hydride to produce products **16H** and **16D** should be virtually identical. Therefore, the rate of formation of **16H** and **16D** can be used as a standard for comparison with the rate of β-sulfonyl hydrogen abstraction. The reactions were carried out in NMR tubes, and the relative amounts of products **16** and **17** produced in each reaction were determined by ^1H NMR integration. The ratio of **16H** to **17H** was 1:6.7

(9) (a) Ueno, Y.; Aoki, S.; Okawara, M. *J. Am. Chem. Soc.* **1979**, *101*, 5414. (b) Watanabe, Y.; Ueno, Y.; Araki, T.; Endo, T.; Okawara, M. *Tetrahedron Lett.* **1986**, *27*, 215.

(10) Iwao, M.; Iihama, T.; Mahalanabis, K. K.; Perrier, H.; Snieckus, V. *J. Org. Chem.* **1989**, *54*, 24.

(11) Harvey, I. W.; Whitham, G. H. *J. Chem. Soc., Perkin Trans. 1* **1993**, 191.

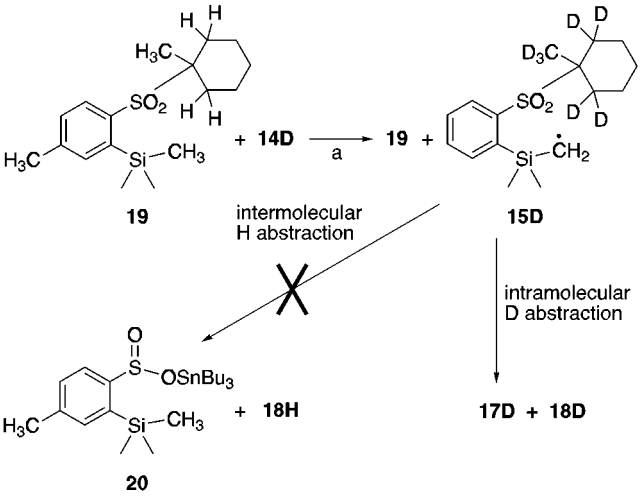
Scheme 3[a]



16H : **17H** = 1 : 6.7 Relative rate of β-abstraction
16D : **17D** = 1 : 0.54 H : D = 6.7 : 0.54 = ~12 : 1

[a] Reagents and conditions: (a) AIBN (0.3 equiv), Bu_3SnH (2.0 equiv, added over 10 h), C_6D_6, 80 °C, 13 h.

Scheme 4[a]

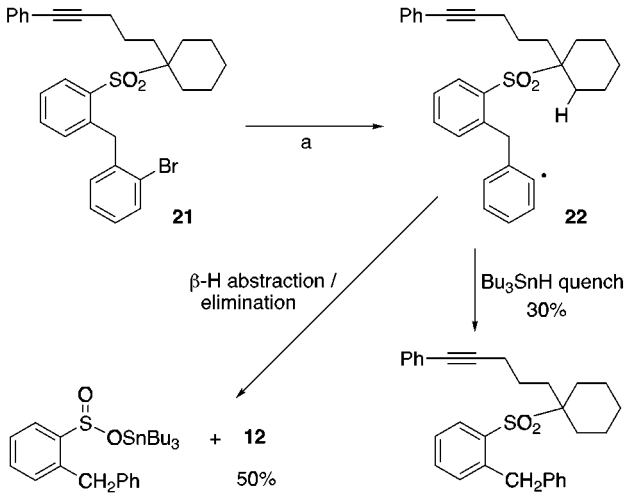


[a] Reagents and conditions: (a) **14D**:**19**, ~1:1, $(Bu_3Sn)_2$ (1.6 equiv based on **14D**), *hν* (350 nm), 26 h.

while the ratio of **16D** to **17D** was 1:0.54. When the product ratios from the two reactions were compared, the relative rate of *β*-sulfonyl H abstraction to D abstraction was determined to be 6.7:0.54 or ~12:1 at 80 °C. A deuterium isotope effect of 12:1 has been reported previously for chlorine radical abstraction of hydrogen from methane-d_2 at 0 °C; however the effect dropped to 7:1 at 71 °C.[12]

A double-labeling study was then devised which took advantage of the large deuterium isotope effect to maximize the potential for intermolecular *β*-sulfonyl hydrogen abstraction by placing intramolecular deuterium abstraction in competition with intermolecular hydrogen abstraction (Scheme 4). Compounds **14D** and **19** were irradiated as a ~1:1 mixture in the presence of bis(tributyltin). In this case, compound **19** is incapable of any intramolecular reaction so any formation of products **20** and **18H** would have to result from intermolecular abstraction of a *β*-sulfonyl hydrogen on **19** by radical intermediate **15D**. Under these conditions, only products **17D** and **18D** were observed along with unreacted **19**, suggesting that no observable intermolecular *β*-sulfonyl hydrogen abstraction was occurring. If no intermolecular hydrogen abstraction is observed under such favorable conditions, it is reasonable to conclude that under "normal" conditions the *β*-sulfonyl hydrogen abstraction step is strictly intramolecular.

Scheme 5[a]



[a] Reagents and conditions: (a) AIBN (0.4 equiv), Bu_3SnH (2.4 equiv, added over 17 h), C_6D_6, 80 °C, 23 h.

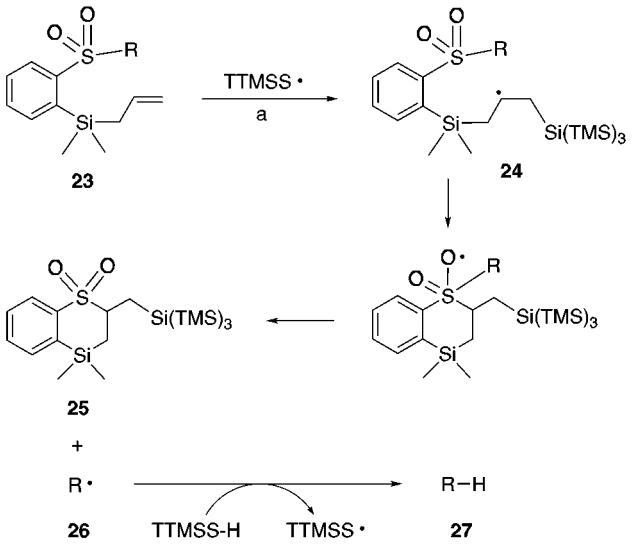
In addition to *o*-silylmethylene radical **2**, reactivities of a number of other carbon-centered radicals with attachments *ortho* to sulfones were examined. *o*-(2-Bromobenzyl)aryl sulfone **21**, when converted to radical intermediate **22**, also suffered intramolecular *β*-hydrogen abstraction (via a 9-membered ring transition state in this instance) followed by sulfonyl radical elimination to afford olefin **12** in 50% NMR yield (Scheme 5). Although addition of tributyltin hydride was slower during the elimination reaction of sulfone **21** than for the analogous reaction of **8a**, intermediate **22** was quenched by tributyltin hydride in 30% NMR yield while intermediate **9** was only quenched in 12% NMR yield (the reactions were carried out at the same concentration). This suggests that the *β*-sulfonyl hydrogen abstraction step is slower for 2-bromobenzyl radical **22** than for silylmethylene radical **9**.

When *o*-(allyldimethylsilyl)aryl sulfone[13] **23** was heated with AIBN and tris(trimethylsilyl)silane (TTMSS-H),[14] addition of the TTMSS radical to the allyl group produced radical intermediate **24** (Scheme 6). Surprisingly, although the secondary radical of intermediate **24** has the same regiochemistry relative to the sulfone as the aryl radical of intermediate **22**, it did not undergo *β*-hydrogen abstraction. Instead, the sulfone group was attacked directly by the radical, causing homolytic sulfone cleavage to afford cyclic sulfone byproduct **25** and reduced product **27** via alkyl radical intermediate **26**. No trace of olefin products was observed.

(12) Wiberg, K. B.; Motell, E. L. *Tetrahedron* **1963**, *19*, 2009.

(13) For preparation of *o*-allyldimethylsilyl aryl sulfones, see ref 7.
(14) Chatgilialoglu, C. *Acc. Chem. Res.* **1992**, *25*, 188.

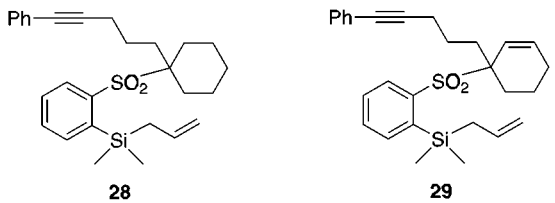
Scheme 6[a]



[a] Reagents and conditions: (a) AIBN (4 equiv), $(TMS)_3SiH$ (5 equiv), toluene-d_8, 111 °C.

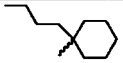
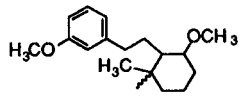
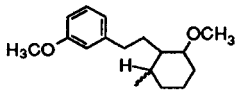
While this reaction will probably not be synthetically useful, due to the reagent cost and the large excess of TTMSS-H required, the difference in reactivity observed for intermediate **24** when compared with **2** or **22** is intriguing. It may result from the added stability of radical **24** imparted by two β-silyl groups.[15] Steric hindrance from the large TTMSS group is also likely to be a factor. Products resulting from TTMSS-H reduction of intermediate **24** were not detected even though the concentration of TTMSS-H was always relatively high (~0.06 M). This suggests that β-TTMSS radical intermediate **24** is sterically protected from attack by the bulky TTMSS-H reagent.

This reaction constitutes a new mode of reductive desulfonylation, and yields (based on formation of cyclic sulfone by-product **25**) are summarized in Table 2. Homolytic sulfone cleavage was even observed with a secondary sulfone (Table 2, entry 3); however, the reaction proceeded at a slower rate and generated a complex mixture of sulfone-cleaved products. Due to the tendency of TTMSS radicals to add to carbon–carbon multiple bonds,[16] a mixture of TTMSS adducts is obtained when unsaturated groups are present in the substrate in addition to the allylsilane moiety such as in compounds **28** and **29**. Further experiments are needed in order to define how the variables of regiochemistry, steric hindrance, and reactivity of the *ortho*-radical species combine to determine the mode of sulfone activation.



Radical-mediated elimination of *o*-[(bromomethyl)silyl]aryl sulfones serves as a complementary procedure to the triflic acid catalyzed elimination of *o*-[(allyldimethylsilyl]aryl sulfones.[7] The reaction should prove to be a useful addition to the limited methods currently available for elimination of unactivated tertiary sulfones.

Table 2. Conditions and Yields for Radical-Mediated Reductive Desulfonylation of *o*-(Allyldimethylsilyl)aryl Sulfones

Entry #	SO_2–R / Si ; R =	Reaction Temp / Time	NMR Yield of by-product **25**
1	 **23a**	111°C / 21 h	66 %
2	 **23b**	111°C / 25 h	62 %[b]
3	 **23c**	111°C / 45 h	64 %[c]

[a] Yields of sulfone-cleaved products (R-H) were difficult to determine accurately by isolation or NMR integration because of interference from a complex mixture of TTMSS decomposition products which formed as the reaction proceeded. [b] Byproduct **25** was isolated in 51% yield from this reaction, and formation of the sulfone-cleaved product (R-H) was verified by GCMS analysis.[c] A complex mixture of sulfone-cleaved products was produced.

Experimental Section

General Methods. See Experimental Section of ref 7 with the following addition: benzene-d_6 and toluene-d_8 were purchased from Cambridge Isotope Laboratories and used without further treatment.

General Workup Procedure. The reaction mixture was poured into a saturated aqueous solution of sodium bicarbonate, and the aqueous phase was extracted three times with CH_2Cl_2. The combined organic phases were dried over $MgSO_4$ and concentrated in vacuo, providing a crude product residue.

General Procedure for Radical-Mediated Sulfone Elimination (Method A). An NMR tube solution containing *o*-[(bromomethyl)dimethylsilyl]aryl sulfone starting material **1** (0.007 M), 1,3,5-trimethoxybenzene (NMR internal standard, 0.3 equiv), and AIBN (0.3 equiv) in benzene-d_6 was deoxygenated by the freeze–pump–thaw method. The reaction mixture was then heated to reflux, and a 0.25 M solution of tributyltin hydride (2.0 equiv) in benzene was added via syringe pump over 10 h. After an additional 3 h at reflux, the yield of the reaction was determined by NMR integration of the olefin product relative to the 1,3,5-trimethoxybenzene internal standard.

General Procedure for Radical-Mediated Sulfone Elimination (Method B). A Pyrex NMR tube solution containing *o*-[(bromomethyl)dimethylsilyl]aryl sulfone starting material **1** (0.025 M), 1,3,5-trimethoxybenzene (NMR internal standard, 0.3 equiv), and bis(tributyltin) (1.5 equiv) in benzene-d_6 was deoxygenated by the freeze–pump–thaw method. The reaction mixture was then irradiated in a Rayonet apparatus using 350 nm lamps, and the progress of the reaction was monitored by NMR. Reactions were typically complete after 18–24 h of irradiation. The yield of the reaction was determined by NMR integration of the olefin product relative to the 1,3,5-trimethoxybenzene internal standard.

Analytical Data for Stannyl Sulfinate 7. ^1H NMR (C_6D_6, as observed during NMR tube reactions): δ 0.4 (s, 9H, chemical shift varies by ±0.05 ppm), 7.07 (t, J = 7.5, 1H), 7.25 (t, J = 7.5, 1H, chemical shift varies by ±0.05 ppm), 7.40 (d, J = 7.5, 1H), 8.27 (d, J = 7.5, 1H, chemical shift varies by ±0.1 ppm), ^1H resonances from the tributylstannyl group overlapped with peaks from other tributylstannyl species present in the reac-

(15) (a) Davidson, I. M. T.; Barton, T. J.; Hughes, K. J.; Ijadi-Maghsoodi, S.; Revis, A.; Paul, G. C. *Organometallics* **1987**, *6*, 644. (b) Auner, N.; Walsh, R.; Westrup, J. *J. Chem. Soc., Chem. Commun.* **1986**, 207. (c) Hwu, J. R.; Patel, H. V. *Synlett* **1995**, 989.

(16) Curran, D. P.; Yoo, B. *Tetrahedron Lett.* **1992**, *33*, 6931.

tion mixture and are not included. MS (CI, isobutane): *m/z* 505 (MH^+, isotope cluster consistent with molecule bearing one tin atom).

General Procedure for *o*-[(Bromomethyl)dimethylsilyl]aryl Sulfones 8a−d. To a stirred 0.3 M solution of aryl sulfone in THF, cooled to −78 °C, was added *n*-butyllithium (1.1 equiv), resulting in a clear, yellow-orange solution. After the solution was stirred for 2.5 h at −78 °C, (bromomethyl)-chlorodimethylsilane (1.3 equiv) was added and the reaction mixture was allowed to warm to 25 °C. After the solution was stirred at 25 °C for 12 h, the clear, light yellow reaction mixture was worked up according to the general procedure, leaving a light yellow oil. The crude product was purified by flash chromatography on silica gel using 7% ethyl acetate in hexane as the eluent.

8a (184 mg, 75% yield, 85% based on recovered starting material): colorless oil; ^{1}H NMR ($CDCl_3$) δ 0.57 (s, 6H), (0.90−1.10 (m, 1H), 1.30−2.17 (m, 13H), 2.43 (t, J = 6.7), 2.92 (s, 2H), 7.27−7.68 (m, 7H), 7.85 (d, J = 7.5, 1H), 7.94 (d, J = 7.7, 1H); ^{13}C NMR ($CDCl_3$) δ −0.2 (o), 19.8 (e), 19.9 (e), 21.5 (e), 22.7 (e), 24.6 (e), 28.5 (e), 29.5 (e), 68.0 (e), 81.3 (e), 89.5 (e), 123.8 (e), 127.6 (o), 128.2 (o), 129.6 (o), 131.5 (o), 132.1 (o), 132.5 (o), 137.4 (o), 138.8 (e), 141.4. (e); MS (CI, isobutane) *m/z* 517/519 (MH^+).

8b (285 mg, 85% yield): white crystals, mp 47−49 °C; ^{1}H NMR ($CDCl_3$) δ 0.56 (s, 6H), 0.86 (t, J = 6.8, 3H), 0.90−1.08 (m, 1H), 1.20−1.42 (m, 6H), 1.45−1.70 (m, 5H), 1.81−1.92 (m, 4H), 2.91 (s, 2H), 7.54−7.65 (m, 2H), 7.83−7.93 (m, 2H); ^{13}C NMR ($CDCl_3$) δ −0.3 (o), 13.9 (o), 19.8 (e), 21.6 (e), 23.3 (e), 24.6 (e), 25.5 (e), 29.1 (e), 29.5 (e), 68.2 (e), 129.5, (o), 132.0 (o), 132.3 (o), 137.3 (o), 138.7 (e), 141.8 (e); MS (CI, isobutane) *m/z* 431/433 (MH^+).

8c (92 mg, 81% yield): colorless oil; ^{1}H NMR ($CDCl_3$) δ 0.57 (s, 6H), 1.37 (s, 6H), 2.02−2.10 (m, 2H), 2.64−2.72 (m, 2H), 2.92 (s, 2H), 7.15−7.24 (m, 3H), 7.29 (t, J = 7.5, 2H), 7.56−7.67 (m, 2H), 7.87 (d, J = 7.1, 1H), 7.94 (d, J = 7.3, 1H); ^{13}C NMR ($CDCl_3$) δ −0.3 (o), 19.7 (e), 21.6 (o), 30.4 (e), 37.3 (e), 64.6 (e), 126.1 (o), 128.2 (o), 128.5 (o), 129.7 (o), 131.9 (o), 132.6 (o), 137.4 (o), 138.9 (e), 141.0 (e, 2 carbons, not resolved); MS (CI, isobutane) *m/z* 439/441 (MH^+).

8d (337 mg, 87% yield): white crystals, mp 58−60 °C; ^{1}H NMR ($CDCl_3$) δ 0.55 (s, 6H), 1.32 (s, 9H), 2.91 (s, 2H), 7.55−7.66 (m, 2H), 7.85 (d, J = 7.1, 1H), 7.92 (d, J = 7.3, 1H); ^{13}C NMR ($CDCl_3$) δ −0.41 (o), 19.6 (e), 24.2 (o), 61.3 (e), 129.6 (o), 131.8 (o), 132.5 (o), 137.3 (o), 138.7 (e), 140.7 (e); MS (CI, isobutane) *m/z* 349/351 (MH^+).

Olefin Product 12. A solution containing *o*-[(bromomethyl)dimethylsilyl]aryl sulfone starting material **8a** (40 mg, 0.077 mmol) and AIBN (3.8 mg, 0.023 mmol) in benzene (11 mL) was deoxygenated by the freeze−pump−thaw method. The reaction mixture was then heated to reflux, and 0.62 mL of a 0.25 M solution of tributyltin hydride in benzene was added via syringe pump over 10 h. After an additional 3 h at reflux, the reaction mixture was concentrated in vacuo and the colorless residue was purified by flash chromatography on silica gel using 100% hexane as the eluent to afford 11 mg (63% yield) of **12**: colorless oil; ^{1}H NMR ($CDCl_3$) δ 1.39−2.10 (m, 12H), 2.25 (t, J = 6.7, 2H), 5.43 (s, 1H), 6.93−7.03 (m, 3H), 7.50 (d, J = 7.4, 2H); MS (EI) *m/z* 224 (M^+).

***β*-Deuterated *o*-[(Bromomethyl)dimethylsilyl]aryl Sulfone 14D.** To a solution of 1-(phenylsulfonyl)-2,2,6,6-tetradeuteriocyclohexane (0.875 g, 3.83 mmol) in THF (11 mL) which had been cooled to −78 °C, was added *n*-butyllithium (4.02 mmol). After the solution was stirred at −78 °C for 1.5 h, CD_3I (Aldrich, 0.262 mL, 4.21 mmol) was added and the reaction was allowed to warm to 25 °C. After 19 h, the reaction mixture was cooled back to −78 °C and *n*-butyllithium (4.21 mmol) was added. After an additional 1.5 h at −78 °C, the reaction was quenched with (bromomethyl)chlorodimethylsilane (0.679 mL, 4.98 mmol) and allowed to warm to 25 °C. After 2 h of stirring at 25 °C, the reaction mixture was worked up according to the general procedure and the crude product purified by flash chromatography on silica gel to afford 1.01 g (65% yield) of a ∼2:1 mixture of *o*-(bromomethyl)silyl and *o*-(iodomethyl)silyl products. The product mixture (300 mg, 0.732 mmol) was then dissolved in methanol (20 mL), and NaBr (3.12 g, 30.3 mmol) was added, resulting in a clear, colorless solution after several minutes of stirring. The reaction mixture was heated to reflux (65 °C) for 90 h, resulting in little change in appearance, and then concentrated in vacuo and worked up according to the general procedure to afford 212 mg (73% yield) of pure (bromomethyl)silyl product **14D**: light yellow oil; ^{1}H NMR ($CDCl_3$) δ 0.55 (s, 6H), 1.01−1.19 (m, 1H), 1.24−1.38 (m, 2H), 1.59−1.74 (m, 3H), 2.91 (s, 2H), 7.53−7.65 (m, 2H), 7.82−7.92 (m, 2H) ^{13}C NMR ($CDCl_3$) δ −0.3 (o), 19.7 (e), 21.3 (e), 24.8 (e), 129.5 (o), 131.9 (o), 132.4 (o), 137.3 (o), 138.9 (e), 140.6 (e); MS (CI, isobutane) *m/z* 396/398 (MH^+).

***o*-[(Bromomethyl)dimethylsilyl]aryl Sulfone 14H.** The procedure outlined for the preparation of **14D** was followed using phenyl cyclohexyl sulfone as the starting material to afford 268 mg (66% overall yield based on phenyl cyclohexyl sulfone) of **14H**: colorless oil; ^{1}H NMR ($CDCl_3$) δ 0.56 (s, 6H), 1.02−1.20 (m, 1H), 1.24 (s, 3H), 1.24−1.43 (m, 2H), 1.59−1.90 (m, 7H), 2.91 (s, 2H), 7.53−7.65 (m, 2H), 7.82−7.92 (m, 2H); ^{13}C NMR ($CDCl_3$) δ −0.3 (o), 17.3 (o), 19.7 (e), 21.5 (e), 24.9 (e), 30.1 (e), 65.2 (e), 129.5 (o), 131.9 (o), 132.4 (o), 137.3 (o), 138.9 (e), 140.6 (e); MS (CI, isobutane) *m/z* 389/391 (MH^+).

***o*-(Trimethylsilyl)aryl Sulfone 19.** Compound **19** was prepared by reducing the corresponding *o*-[(iodomethyl)dimethylsilyl]aryl sulfone with tributyltin hydride. Conditions were chosen to favor reduction over elimination via *β*-sulfonyl hydrogen abstraction. A solution containing *o*-[(iodomethyl)dimethylsilyl]aryl sulfone starting material (250 mg, 0.555 mmol), AIBN (0.062 mmol), and tributyltin hydride (0.833 mL, 3.10 mmol) in benzene (5 ml) was deoxygenated by the freeze−pump−thaw method. The reaction mixture was heated to reflux for 6 h and then concentrated in vacuo, and the residue was purified by flash chromatography on silica gel using 7% ethyl acetate in hexane as the eluent to afford 152 mg (84% yield) of **19**: colorless oil; ^{1}H NMR ($CDCl_3$) δ 0.39 (s, 9H), 1.00−1.20 (m, 1H), 1.22 (s, 3H), 1.25−1.43 (m, 2H), 1.57−1.75 (m, 5H), 1.77−1.89 (m, 2H), 2.41 (s, 3H), 7.30 (d, J = 8.0, 1H), 7.60 (s, 1H), 7.75 (d, J = 8.0, 1H); ^{13}C NMR ($CDCl_3$) δ 2.0 (o), 17.2 (o), 21.5 (e), 21.6 (o), 25.0 (e), 30.1 (e), 64.7 (e), 129.3 (o), 132.0, (o), 137.3 (e), 137.6 (o), 142.6 (e), 142.7 (e); MS (CI, isobutane) *m/z* 309 (M^+-CH_3).

***o*-(2-Bromobenzyl)aryl Sulfone 21.** The general procedure described above for the synthesis of *o*-[(bromomethyl)dimethylsilyl]aryl sulfones **8a−d** was followed except 2-bromobenzyl bromide (5 equiv) was used instead of (bromomethyl)chlorodimethylsilane as the electrophile. **21** (75 mg, 25% yield): colorless oil; ^{1}H NMR ($CDCl_3$) δ 1.00−1.18 (m, 1H), 1.35−1.55 (m, 2H), 1.59−1.85 (m, 5H), 1.87−2.12 (m, 6H), 2.46 (t, J = 6.5, 2H), 4.65 (s, 2H), 7.03−7.14 (m, 3H), 7.21 (t, J = 7.5, 1H), 7.25−7.42 (m, 6H), 7.46 (t, J = 7.6, 1H), 7.58 (d, J = 7.9, 1H), 7.99 (d, J = 7.9, 1H); ^{13}C NMR ($CDCl_3$) δ 19.9 (e), 21.5 (e), 22.8 (e), 24.7 (e), 28.4 (e), 29.0, (e), 38.9 (e), 67.5 (e), 81.3 (e), 89.5 (e), 123.8 (e), 124.8 (e), 126.6 (o), 127.6 (o), 127.7 (o), 128.1 (o), 128.2 (o), 131.5 (o), 131.6 (o), 131.8 (o), 132.7 (o) , 133.5 (o), 133.6 (o), 134.0 (e), 139.8 (e), 142.0 (e); MS (CI, isobutane) *m/z* 535/537 (MH^+).

***o*-(Allyldimethylsilyl)aryl sulfones 23a−c.** See ref 7 for preparation and characterization of *o*-(allyldimethylsilyl)aryl sulfones.

General Procedure for Radical-Mediated Reductive Desulfonylation of *o*-(Allyldimethylsilyl)aryl Sulfones. An NMR tube solution containing *o*-(allyldimethylsilyl)aryl sulfone starting material **23** (0.03 M), AIBN (0.5 equiv), and tris(trimethylsilyl)silane (TTMSS) (2.0 equiv) in toluene-d_8 (1 mL) was deoxygenated by the freeze−pump−thaw method and then heated to reflux (110 °C). The progress of the reaction was monitored by NMR, and additional aliquots of AIBN (0.5 equiv) and TTMSS (0.5 equiv) were added at 3−5 h intervals until the reaction was complete (reaction times were typically 20−26 h for tertiary sulfones, 40−48 h for secondary sulfones). Yields of the cyclic sulfone byproduct **25** were based on NMR integration, and structures of desulfonylated products were determined by GC/MS analysis.

Cyclic Sulfone Byproduct 25. The general procedure described for radical-mediated reductive desulfonylation was followed using **23b** (17 mg, 34 μmol) as the starting material. When the reaction was complete by NMR, the reaction mixture

was concentrated in vacuo and the colorless residue purified by flash chromatography on silica gel using 100% hexane as the eluent to afford 9 mg (51% yield) of **25**: white crystals, mp 65−67 °C; ^{1}H NMR ($CDCl_3$) δ 0.21 (s, 27H), 0.27 (s, 3H), 0.36 (s, 3H), 0.71 (dd, J = 4.8, 14.5, 1H), 0.93 (dd, J = 12.3, 14.3, 1H), 1.28 (dd, J = 8.1, 14.5, 1H), 1.53 (dd, J = 2.1, 14.3, 1H), 3.30 (dddd, J = 2.1, 4.8, 8.1, 12.3, 1H), 7.21 (br,t, J = 7.3, 1H), 7.28 (br,d, J = 7.3, 1H), 7.35 (br,t, J = 7.3, 1H), 7.50 (br,d, J = 7.3, 1H); ^{13}C NMR ($CDCl_3$) δ −1.6 (o), −0.2 (o), 1.5 (o, 9 carbons), 20.2 (e), 21.5 (e), 43.6 (o), 124.8 (o), 125.8 (o), 129.7 (o), 131.8 (o), 138.8 (e), 159.6 (e); MS (EI) m/z 349, 175, 73.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of new compounds described in the text (20 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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