Sulfones as Radical Progenitors: An Unprecedented Example of Homolytic Sulfone Cleavage Facilitated by *o*-Stannyl Substitution of Aryl Sulfones[1]

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Allylic aryl sulfones bearing an *o*-allyldialkylstannyl moiety (**1b**), when converted to stannyl radical **1a**, suffer homolytic cleavage via intramolecular attack of the stannyl radical on the sulfone. Allyl radicals generated in this manner can be utilized for further intramolecular radical cyclizations; thus the overall transformation can be viewed as an alkylative desulfonylation reaction. Previously unknown sulfonyl stannane polymer **5** is generated as a byproduct. The *o*-dibutylstannyl radical derived from nonallylic aryl sulfone **15** does not suffer homolysis but instead forms 9-membered macrocycle **19** via an intramolecular reaction with the phenylacetylene group.

Introduction

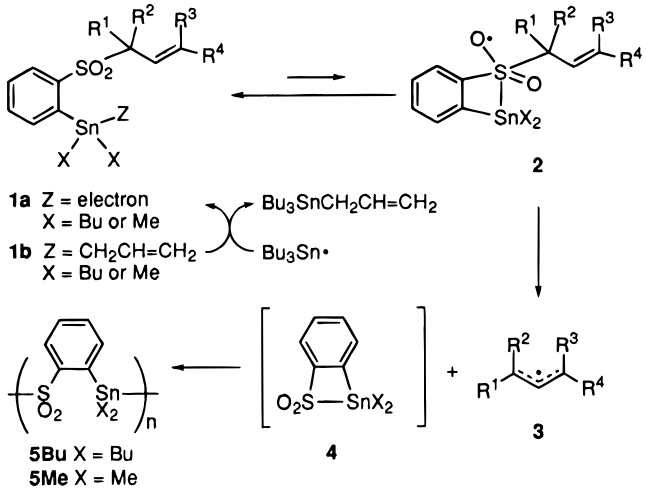
Allylic aryl sulfones serve as valuable synthetic intermediates for the formation of carbon−carbon bonds via alkylation reactions of α-sulfonyl anions. Once having facilitated bond formation, a variety of desulfonylation methods are available to allylic sulfones. These include substitution with organometallic reagents and reduction or substitution after π-allyl complex formation.[2] S_H' displacement of allylic sulfones is also well-known;[3] however the reaction appears to be limited to terminal olefins and does not generate alkyl radical intermediates upon homolytic sulfone cleavage. To our knowledge, there are no desulfonylation methods which produce usable radical intermediates upon sulfone removal.

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 cleave under mild conditions to afford olefins.[4] Herein we report an unprecedented mode of homolytic aryl sulfone cleavage, promoted by an *o*-stannyl moiety, which produces allyl radical intermediates capable of further intramolecular cyclization reactions.

Results and Discussion

It has been discovered that aryl sulfones bearing an *o*-allyldialkylstannyl moiety **1b**, upon heating with AIBN and tributyltin hydride, suffer homolytic cleavage to afford allyl radical **3** and polymer byproduct **5** (Scheme 1). Allyl radicals generated in this manner can be utilized for further intramolecular radical cyclizations as demonstrated by the formation of compound **13** in 99% NMR yield (Scheme 3). Thus the overall transformation can be viewed as an alkylative desulfonylation reaction. It is proposed that the reaction proceeds via intermediate

Scheme 1



2 resulting from intramolecular stannyl radical attack on the sulfone. Heterocycle **4** is believed to be the initial short lived byproduct, formed after sulfone cleavage, which rapidly polymerizes to afford the previously unknown isolated byproduct **5**. Only the broadened ^{1}H NMR peaks of polymer **5** are observed during NMR tube reactions.

Introduction of the *o*-allyldialkylstannyl moiety could be accomplished using similar methodology to that described previously for the introduction of an *o*-allyldimethylsilyl group.[4] Thus, *o*-metalation of phenylsulfones bearing no acidic α-protons with *n*-butyllithium[5] followed by treatment with distilled allyldibutylchlorostannane afforded *o*-stannylated sulfones in 70−89% yield.

Mercaptide anion **6** (prepared in one pot from thiophenol)[6] is a more versatile precursor for the preparation of allylic aryl sulfones bearing an *o*-stannyl group allowing attachment of the *o*-stannyl group prior to introduction of the aryl sulfone (Scheme 2). For example, by treating **6** *in situ* with 2-bromocyclohexene, *o*-stannyl phenyl sulfide derivative **7** was obtained in 49% overall yield based on thiophenol. While the use of peracids for oxidation of sulfide **7** to sulfone **8** was unsuccessful due

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(1) Synthesis via Vinyl Sulfones. 72.

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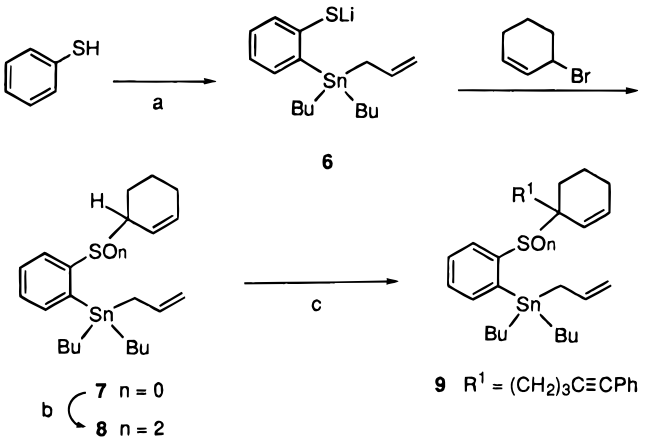
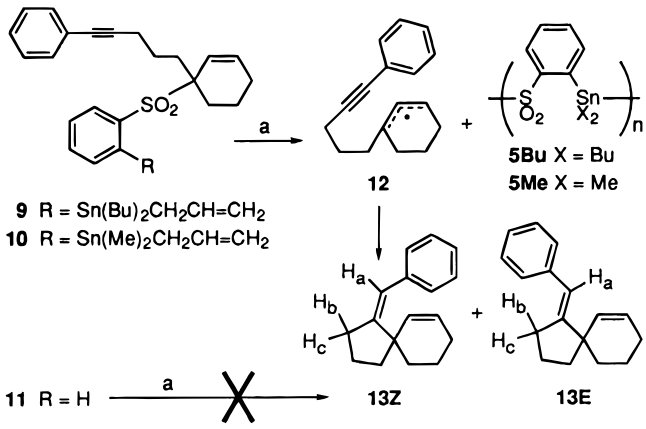
Scheme 2[a]



[a] Reagents and conditions: (a) TMEDA (2.2 equiv), *n*-BuLi (2.2 equiv), cyclohexane, −40 to 25 °C, 24 h, then $ClSn(Bu)_2CH_2CH{=}CH_2$, 1:1 cyclohexane: THF, −78 to 25 °C; (b) CH_3CN (10 equiv), K_2CO_3 (0.7 equiv), H_2O_2 (6 equiv), MeOH, 25 °C, 1 h (79%); (c) lithium diisopropylamide (1.1 equiv), THF, −78 °C, 1 h, $PhC{\equiv}C(CH_2)_3I$ (1.1 equiv), −78 to 25 °C, 18 h (83%).

Scheme 3[a]



[a] Reagents and conditions: AIBN (0.3 equiv), Bu_3SnH (1.8 equiv), C_6D_6, 80 °C.

to competitive protiodestannylation, conversion of **7** to **8** was achieved in 79% yield using peroxyimidic acid[7] as the oxidant. Carbon−carbon bond formation at the α-position was readily accomplished via metalation with lithium diisopropylamide followed by reaction with (5-iodo-1-pentynyl)benzene[8] to provide **9** in 83% yield.

An NMR study was carried out by heating **9**, **10**, and **11** in three separate NMR tubes with AIBN and tributyltin hydride in benzene-d_6 (Scheme 3). Homolytic sulfone cleavage appeared to be quantitative by NMR for starting materials **9** and **10** with no trace of products resulting from S_H' displacement of the sulfone by tributyltin radicals being observed. Under identical reaction conditions, no trace of sulfone cleaved product **13** was observed in a control experiment using the nonstannylated phenyl sulfone **11** as starting material. Instead, a mixture of products resulting from the addition of tributyltin radicals to unsaturated sites on **11** appeared to form.

Allyl radical **12** cyclized regioselectively to afford product **13** in 82% isolated yield from starting material **10** (99% NMR yield of **13** from either **9** or **10**). Early in the reaction, isomer **13Z** was the exclusive product observed. As the reaction proceeded, isomer **13E**, presumably resulting from stannyl radical-mediated isomerization of the exocyclic olefin, became a significant product. If the reaction mixture was heated to reflux for a total of 25 h the ratio of **13Z** to **13E** was 3:7 (the sulfone cleavage reaction generally reached completion within 12 h). Assignment of *E* and *Z* isomers of **13** was based on the coupling constants observed between the exocyclic olefin proton (H_a) and the two allylic protons H_b and H_c. In the ^1H NMR spectrum of **13Z**, H_a appears as a slightly broadened singlet whereas H_a in the ^1H NMR spectrum of **13E** appears as a triplet with a coupling constant of 2.5 Hz. In similar ring systems bearing exocyclic olefins, the *transiod* allylic coupling constants are reported to be consistently larger than the *cisoid* coupling constants.[9] Therefore, the *E* isomer of **13** is expected to have the larger allylic coupling constant.

Polymeric byproducts **5Bu** and **5Me** could be isolated from starting materials **9** and **10**, respectively. Upon concentration, **5Bu** hardens into a flexible glassy solid which readily redissolves in solvents such as benzene, chloroform, and methanol, while **5Me** becomes increasingly insoluble over time. NMR evidence suggests that sulfone rather than sulfinate linkages exist in the polymer backbone of **5Bu**. A stannyl sulfinate linkage would cause the two butyl groups attached to tin to be diastereotopic while a stannyl sulfone linkage would result in symmetry equivalent butyl groups. In both the ^1H and ^{13}C NMR spectra of **5Bu**, all peaks are broadened due to its polymeric structure but only one set of butyl peaks is observed. The stannyl methyl groups of **5Me** also produce a single broadened ^1H NMR peak but were difficult to observe by ^{13}C NMR due the low solubility of **5Me**. While not conclusive, this appears to be more consistent with a stannyl sulfone linkage than a stannyl sulfinate linkage in the polymer backbone.

In contrast to the homolytic cleavage observed for allyl sulfones, non-allylic aryl sulfones bearing an *o*-dialkylstannyl radical did not suffer homolysis under similar conditions (Scheme 4). When compound **14**, containing no intramolecular radical acceptor, was heated with AIBN and tributyltin hydride, the *o*-stannyl radical **16** was simply quenched by tributyltin hydride producing sulfone-bearing tin hydride **18** in 90% NMR yield. However, when compound **15** was heated with AIBN and tributyltin hydride, the *o*-stannyl radical **17** reacted intramolecularly with the phenylacetylene group to afford 9-membered macrocycle **19** in 86% isolated yield.

Molecular modeling studies (Cache v. 3.5) of intermediate **17** suggested that in the most stable conformation the acetylene moiety was positioned only ∼3 Å away from the *o*-stannyl radical. As previously observed in the X-ray crystal structure of an *o*-(allyldimethylsilyl)aryl sulfone,[4] the X-ray crystal structure of **19** (Figure 1) revealed a significant sulfone oxygen−*o*-metal interaction with a Sn−O distance of 2.9 Å (the sum of the van der Waals radii of Sn and O is ∼3.7 Å[10]). While 9-membered ring formation is typically a relatively slow process,[11] a

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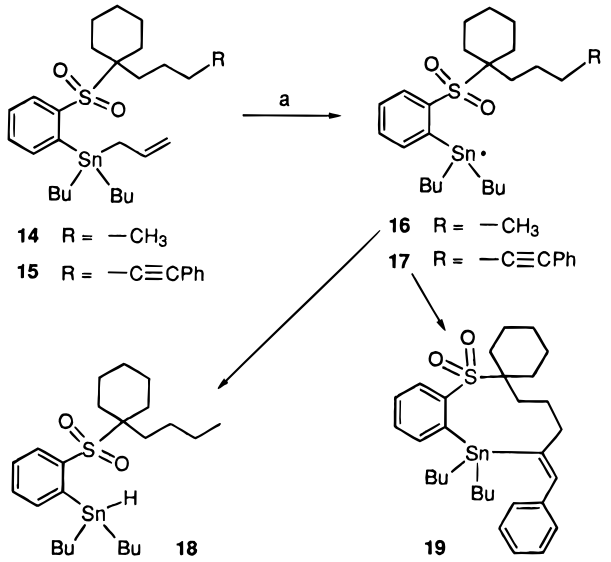
Scheme 4[a]



[a] Reagents and conditions: AIBN (0.2−1.0 equiv), Bu_3SnH (1.2−1.8 equiv), C_6D_6, 80 °C.

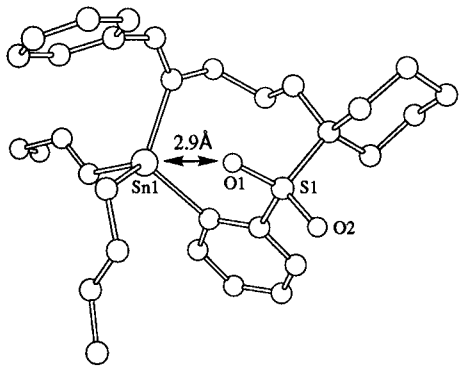


Figure 1. X-ray crystal structure of **19** showing Sn−sulfone oxygen interaction.

similar tin−oxygen association in radical intermediate **17** along with the quaternary sulfone-bound carbon probably contribute to the rigidity and preorganization of the system making cyclization more facile. It is likely that the *o*-stannyl radicals derived from both allylic sulfone **9** and saturated sulfone **15** react reversibly with the sulfonyl moiety to form intermediates similar to **2**. However, in the case of allylic sulfone **9**, the rate of homolytic sulfone cleavage is sufficiently rapid that there is minimal chance for reaction between the *o*-stannyl radical and the phenylacetylene group.

Removal of allylic sulfones via *o*-tin radical assisted homolytic cleavage constitutes a new method for generating allyl radicals. When this is coupled with the activating ability of the arylsulfonyl group toward α-carbon−carbon bond formation, it should prove to be a useful synthetic tool. Extension of the *o*-substitution strategy for activating tertiary and secondary aryl sulfones toward homolytic cleavage is being investigated.

Experimental Section

General Methods. See Experimental Section of ref 4 with the following addition: deuterated benzene was 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.

Stannyl Sulfone Polymer 5Bu. The procedure described for the preparation of **13** was carried out using the dibutylstannyl starting material **9**. When the reaction was complete, the reaction mixture was concentrated in vacuo and the residue washed with hexane. The glassy solid which remained undissolved in hexane was dissolved in methanol and purified by flash chromatography on normal phase silica gel using 100% methanol as the eluting solvent to afford a pure sample of **5Bu**. A sample of the dimethylstannyl analog **5Me** can be obtained using the same procedure with **10** as the starting material. **5Bu**: colorless glassy solid; ^{1}H NMR ($CDCl_3$) δ 0.79 (br, t, J = 6.6, 6H), 1.10−1.80 (br, m, 12H), 7.35−7.50 (br, m, 2H), 7.56 (br, d, J = 6.5, 1H), 7.91 (br, d, J = 6.5, 1H); ^{13}C NMR (C_6D_6) δ 13.9 (o), 23 (e, highly broadened), 27.2 (e, broadened), 28.4 (e), 126.1 (o), 129.7 (o), 131.2 (o), 137.1 (e), 137.6 (o), 155.6 (e); MS (CI, isobutane) *m*/*z* 747 isotope cluster consistent with compound bearing two tin atoms (weak, MH^+ for dimer), 375 isotope cluster (MH^+ for monomer). **Dimethyl analog 5Me**: colorless glassy solid; ^{1}H NMR ($CDCl_3$) δ 0.67 (br, s, 6H), 7.50 (br, s, 2H), 7.59 (br, s, 1H), 7.93 (br, s, 1H); MS (CI, isobutane) *m*/*z* 291 isotope cluster (MH^+ for monomer).

Allyldibutylchlorostannane (Distilled). To a −78 °C solution of dibutyltin dichloride (Aldrich, 11.42 g, 37.6 mmol) in THF (30 mL) was added allylmagnesium bromide (45.1 mmol) over 5 min. After addition was complete, the reaction mixture was allowed to gradually warm to 25 °C and was stirred at 25 °C for 2h. The THF was then removed by trap to trap distillation, and the residue was distilled under reduced pressure (∼0.3 Torr). A mixture weighing 6.7 g and consisting of 73% allyldibutylchlorostannane and 27% diallyldibutylstannane was collected between 89 and 101 °C (42% yield taking into account the purity of the product). The diallyldibutylstannane impurity did not appear to interfere when the allyldibutylchlorostannane was used in subsequent reactions as an electrophile.

***o*-Stannylaryl Mercaptide 6 and *o*-Stannylaryl Sulfide 7.** To a stirred solution of *n*-butyllithium (3.09 mmol) and tetramethylethylenediamine (0.466 mL, 3.09 mmol) in cyclohexane (3.0 mL), which had been immersed in a dry ice bath for 1 min, was added thiophenol (0.144 mL, 1.40 mmol) resulting in a clear, light yellow solution. The bath was removed, and the reaction mixture was stirred vigorously at 25 °C for 48 h resulting in an opaque, fine off-white slurry[6] (24 h of stirring is sufficient but the slurry remains usable for several days). THF (2.5 mL) was then added, causing the reaction mixture to turn homogeneous and light yellow over 1 min. The reaction mixture was then immediately cooled to −78 °C, and distilled allyldibutylchlorostannane (1.8 mmol) was added to afford mercaptide **6**. After the solution was stirred at −78 °C for 8 min, mercaptide **6** was quenched *in situ* with 3-bromocyclohexene (0.242 mL, 2.10 mmol). The clear, light yellow reaction mixture was then allowed to warm to 25 °C and, after being stirred at 25 °C for 12 h, 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 100% hexane as the eluent, to afford 321 mg (49% yield based on the limiting reagent, thiophenol) of **7**: colorless oil; ^{1}H NMR ($CDCl_3$) δ 0.91 (t, J = 7.3, 6H), 1.07−1.28 (m, 4H), 1.29−1.43 (m, 4H), 1.44−1.74 (m, 5H), 1.75−2.25 (m, 7H), 3.87 (br, s, 1H), 4.72 (br, d, J = 10.0, 1H), 4.89 (br, d, J = 16.9, 1H), 5.76 (ddt, J = 3.6, 10.0, 1.8, 1H), 5.85 (ddt, J = 1.1, 10.0, 3.6, 1H), 6.03 (ddt, J = 10.0, 16.9, 8.1, 1H), 7.20 (dt, J = 1.2, 7.2, 1H), 7.29 (dt, J = 1.7, 7.6, 1H), 7.41 (dd J = 1.7, 7.2, 1H), 7.49 (dd, J = 0.8, 7.6, 1H); ^{13}C NMR ($CDCl_3$) δ 11.3 (e), 13.7 (o), 18.1 (e), 19.7 (e), 25.0 (e), 27.3 (e), 29.0 (e, 2 carbons, not resolved), 45.1 (o), 110.1 (e), 126.1 (o), 126.9 (o), 129.0 (o), 130.1 (o), 130.8 (o), 136.7 (o), 137.7 (o), 143.9 (e), 147.0 (e); MS (CI, isobutane) *m*/*z* 465 isotope cluster (MH^+, weak), 423 isotope cluster ($MH^+ - C_3H_6$).

***o*-Stannylaryl Sulfone 8.** To a stirred solution of **7** (1.57 g, 3.39 mmol) in CH_3OH (15 mL) was added (in order) CH_3CN (1.77 mL, 33.9 mmol), K_2CO_3 (0.33 g, 2.4 mmol), and 70% H_2O_2 (0.63 mL, 16.9 mmol) at 0 °C. After 5 min, the ice bath was

removed and the reaction mixture was stirred without cooling for 1.5 h (some heat was evolved). At this point, the reaction was not complete by TLC analysis, so an additional portion of 70% hydrogen peroxide (0.12 mL, 3.3 mmol) was added and the reaction mixture was stirred for 1 h at 25 °C resulting in completion of the reaction as observed by TLC. Dimethyl sulfide (0.72 mL, 9.83 mmol) was then added to quench any residual peroxides. After being stirred at 25 °C for 15 min, the reaction mixture was concentrated in vacuo and the residue purified by flash chromatography on silica gel using 10% ethyl acetate in hexane as the eluent to afford 1.32 g (79% yield) of **8**: colorless oil; ^{1}H NMR ($CDCl_3$) δ 0.86 (t, J = 7.3, 3H), 0.87 (t, J = 7.3, 3H), 1.05−1.38 (m, 8H), 1.40−1.66 (m, 5H), 1.80−2.23 (m, 7H), 3.70 (br, s, 1H), 4.70 (br, d, J = 10.0, 1H), 4.87 (br, d, J = 16.8, 1H), 5.62 (ddd, J = 2.1, 2.5, 10.2, 1H), 5.90−6.18 (m, 2H), 7.45−7.62 (m, 2H), 7.75 (dd, J = 1.5, 7.2, 1H), 7.93 (dd, J = 1.4, 7.5, 1H); ^{13}C NMR ($CDCl_3$) δ 12.5 (e), 13.6 (o), 19.1 (e), 19.5 (e), 22.0 (e), 24.5 (e), 27.2 (e), 28.9 (e), 61.2 (o), 110.3 (e), 118.1 (o), 128.7 (o), 129.7 (o), 132.2 (o), 135.6 (o), 137.8 (o), 137.9 (o), 143.2 (e), 144.4 (e); MS (CI, isobutane) m/z 455 isotope cluster ($MH^+ - C_3H_6$).

***o*-Stannylaryl Sulfone 9 via α-Metalation Followed by Electrophile Quench.** To a stirred solution of *o*-stannylaryl sulfone **8** (489 mg, 0.986 mmol) in THF (8.5 mL), cooled to −78 °C, was added a solution of lithium diisopropylamide (1.09 mmol) in THF (4.5 mL) resulting in a clear, bright orange solution. After 1.0 h of stirring at −78 °C, $PhC{\equiv}C(CH_2)_3I$[8] (1.09 mmol) was added and the reaction mixture was allowed to warm to 25 °C. After 18 h of stirring at 25 °C, 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 6% ethyl acetate and 2% triethylamine in hexane as the eluent to afford 523 mg (83% yield) of **9**: colorless oil; ^{1}H NMR (C_6D_6) δ 0.89 (t, J = 7.2, 3H), 0.91 (t, J = 7.2, 3H), 1.00−1.85 (m, 20H), 1.86−2.40 (m, 6H), 4.88 (br, d, J = 10.0, 1H), 5.07 (br, d, J = 16.8, 1H), 5.55−5.80 (m, 2H), 6.18 (ddt, J = 10.0, 16.8, 8.1, 1H), 6.90−7.05 (m, 4H), 7.11 (t, J = 7.3, 1H), 7.40−7.50 (m, 2H), 7.72 (d, J = 7.3, 1H), 7.94 (d, J = 7.7, 1H); ^{13}C NMR (C_6D_6) δ 13.36 (e), 13.43 (e), 13.93 (o), 13.95 (o), 19.0 (e), 20.0 (e), 20.1 (e), 24.0 (e), 24.2 (e), 27.70 (e), 27.74 (e), 27.9 (e), 29.38 (e), 29.41 (e), 34.9 (e), 67.2 (e), 82.0 (e), 89.8 (e), 110.7 (e), 124.6 (e), 125.2 (o), 127.8 (o), 128.3 (o), 128.5 (o), 131.8 (o), 131.9 (o), 132.0 (o), 134.9 (o), 137.7 (o), 138.3 (o), 142.7 (e), 146.1 (e); MS (CI, isobutane) m/z 597 isotope cluster ($MH^+ - C_3H_6$).

***o*-Stannylaryl Sulfone 9 via *Ortho*-metalation Followed by Allyldibutylchlorostannane Quench.** To a stirred solution of phenyl sulfone **11** (365 mg, 0.836 mmol) in THF (5 mL), cooled to −78 °C, was added *n*-butyllithium (0.920 mmol), resulting in a clear, bright orange solution. After 1.5 h at of stirring −78 °C, distilled allyldibutylchlorostannane (1.09 mmol) was added and the reaction mixture was allowed to warm to 25 °C. After 18 h of stirring at 25 °C, 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 5% ethyl acetate in hexane as the eluent to afford 379 mg of **9** and 61 mg of starting material **11** (71% yield, 89% yield based upon recovered starting material).

***o*-(Allyldimethylstannyl)aryl Sulfone 10.** Generally, higher yields were obtained when the allyldialkylchlorostannane species was purified by distillation prior to use as in the previously described synthesis of **9**. However an alternative procedure using the allyldialkylchlorostannane species *in situ* may be more convenient and is described below.

First, a 0.40 M solution of allyldimethylchlorostannane was prepared by adding allylmagnesium bromide (10.7 mL of a 1.0 M solution in diethyl ether) to a solution of dimethyltin dichloride (1.98 g, 9.01 mmol) in diethyl ether (40 mL) which was cooled to 0 °C. The reaction mixture was then allowed to warm to 25 °C. After 1 h at 25 °C, the magnesium salts were filtered under argon, leaving a clear, colorless solution of allyldimethylchlorostannane which was used *in situ* in the following reaction.

Next, *n*-butyllithium (0.894 mmol) was added to a stirred solution of phenyl sulfone **11** (296 mg, 0.812 mmol) in THF (4 mL) which was cooled to −78 °C, resulting in a clear, bright orange solution. After 1.5 h of stirring at −78 °C, this orange solution was transferred via canula to the previously prepared solution of allyldimethylchlorostannane (7.6 mL of a 0.14 M solution in diethyl ether) which was also cooled to −78 °C. The resulting colorless reaction mixture was allowed to warm to 25 °C and, after 1 h of stirring at 25 °C, was worked up according to the general procedure, leaving a faint yellow oil. The crude product was purified by flash chromatography on silica gel using 14% ethyl acetate and 1% triethylamine in hexane as the eluent to afford 231 mg of **10** and 82 mg of starting material **11** (51% yield, 71% yield based upon recovered starting material). **10**: colorless oil; ^{1}H NMR (C_6D_6) δ 0.480 (s, 3H), 0.482 (s, 3H), 1.00−1.65 (m, 8H), 1.85−2.30 (m, 6H), 4.83 (br, d, J = 10.2, 1H) 4.97 (br, d, J = 16.9, 1H), 5.64 (d, J = 10.3, 1H), 5.72 (dt, J = 10.2, 3.6, 1H), 6.05 (ddt, J = 10.2, 16.9, 8.1, 1H), 6.92−7.12 (m, 5H), 7.42−7.50 (m, 2H), 7.63 (d, J = 7.3, 1H), 7.9 (d, J = 7.7, 1H); ^{13}C NMR (C_6D_6) δ −6.8 (o), −6.6 (o), 19.0 (e), 20.0 (e), 21.8 (e), 24.0 (e), 24.1 (e), 27.7 (e), 34.8 (e), 67.1 (e), 82.0 (e), 89.8 (e), 110.8 (e), 124.5 (e), 125.1 (o), 127.8 (o), 128.4 (o), 128.5 (o), 131.8 (o), 131.9 (o), 132.1 (o), 135.0 (o), 137.4 (o), 137.7 (o), 142.4 (e), 145.9 (e).

Tricyclic Hydrocarbons 13E and 13Z. An NMR tube solution of **10** (9.4 mg, 17.0 μmol), AIBN (2.2 μmol), and tributyltin hydride (3.1 μmol) in benzene-d_6 (1.0 mL) was deoxygenated by the freeze−pump−thaw method. (An NMR tube was used as the reaction vessel in this example to facilitate detailed observation of the reaction by NMR analysis.) The reaction mixture was then heated to reflux, and 100 μL of a solution containing tributyltin hydride (0.31 M) and AIBN (0.051 M) was added via syringe pump over 10 h. Slow addition of tributyltin hydride is not necessary for the sulfone cleavage reaction. It was employed to ensure that allyl radical intermediate **12** cyclizes before it is quenched with tributyltin hydride. After an additional hour at reflux, the reaction mixture was cooled to 0 °C and concentrated in vacuo leaving a colorless oil. Hexane (0.3 mL) was added to the residue, dissolving the hydrocarbon product and leaving the stannyl sulfone polymer byproduct undissolved as a glassy solid. The hexane solution was removed via pipet and purified by flash chromatography on silica gel using 100% hexane as the eluent to afford 3.1 mg (82% yield) of **13** (mixture of *E* and *Z* isomers which can be separated by repeated flash chromatography on silica gel with 100% hexane). Yields of **13** are comparable if the dibutylstannyl starting material **9** is used. **13Z**: colorless liquid; ^{1}H NMR ($CDCl_3$) δ 1.45−2.05 (m, 10H), 2.54−2.67 (m, 2H), 5.52 (br, s, 2H), 6.44 (br, s, 1H), 7.12 (t, J = 7.3, 1H), 7.22 (t, J = 7.3, 2H), 7.35 (d, J = 7.3, 2H); ^{13}C NMR ($CDCl_3$) δ 20.3 (e), 22.6 (e), 24.7 (e), 31.3 (e), 37.7 (e), 42.8 (e), 46.1 (e), 122.6 (o), 124.4 (o), 125.7 (o), 127.3 (o, 2 carbons, not resolved), 129.6 (o, 2 carbons, not resolved), 135.8 (o), 138.0 (e), 153.2 (e); MS (CI, isobutane) m/z 225 (MH^+). **13E**: colorless liquid; ^{1}H NMR ($CDCl_3$) δ 1.5−2.1 (m, 10H), 2.61 (dp, J = 2.5, 8.7, 1H), 2.78 (dtt, J = 17.7, 5.1, 2.5, 1H), 5.41 (dt, J = 10.0, 2.0, 1H), 5.85 (dt, J = 10.0, 3.7, 1H), 6.16 (t, J = 2.5, 1H), 7.11−7.38 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 19.3 (e), 23.0 (e), 25.2 (e), 30.6 (e), 34.7 (e), 40.1 (e), 49.3 (e), 122.2 (o), 125.7 (o), 127.2 (o), 128.1 (o, 2 carbons, not resolved), 128.2 (o, 2 carbons, not resolved), 134.8 (o), 138.8 (e), 153.6 (e); MS (CI, isobutane) m/z 225 (MH^+).

***o*-(Allyldibutylstannyl)aryl Sulfones 14 and 15.** Starting from the corresponding phenyl sulfones, the procedure described for the preparation of **10** was followed except allyldibutylchlorostannane was used *in situ* instead of allyldimethylchlorostannane.

14 (240 mg, 46% yield): colorless oil; ^{1}H NMR ($CDCl_3$) δ 0.86 (t, J = 7.2, 9H), 0.97−1.90 (m, 28H), 2.08 (d, J = 8.5, 2H), 4.69 (br, d, J = 10.0, 1H), 4.86 (br, d, J = 16.8, 1H), 6.00 (ddt, J = 10.0, 16.8, 8.5, 1H), 7.48 (br, t, J = 7.6, 1H), 7.55 (br, t, J = 7.2, 1H), 7.75 (br, d, J = 7.2, 1H), 7.89 (br, d, J = 7.6, 1H); ^{13}C NMR ($CDCl_3$) δ 13.0 (e), 13.7 (o), 13.9 (o), 19.7 (e), 21.6 (e), 23.4 (e), 24.7 (e), 25.5 (e), 27.3 (e), 28.8 (e), 29.2 (e), 67.4 (e), 110.2 (e) 128.3 (o), 131.1 (o), 132.0 (o), 137.7 (o), 138.0

(o), 141.4 (e), 146.2 (e); MS (CI, isobutane) *m*/*z* 513 isotope cluster ($MH^+ - C_3H_6$).

15 (502 mg, 42% yield): colorless oil; ^{1}H NMR ($CDCl_3$) δ 0.86 (t, J = 7.3, 6H), 0.97−1.87 (m, 24H), 1.95−2.21 (m, 4H), 2.43 (t, J = 6.7, 2H), 4.69 (br, d, J = 10.0, 1H), 4.86 (br, d, J = 16.9, 1H), 6.00 (ddt, J = 10.0, 16.9, 8.5, 1H), 7.27−7.32 (m, 3H), 7.35−7.46 (m, 3H), 7.53 (br, t, J = 7.3, 1H), 7.75 (br, d, J = 7.3, 1H), 7.94 (br, d, J = 7.7, 1H); ^{13}C NMR ($CDCl_3$) δ 13.0 (e), 13.7 (o), 19.7 (e), 19.9 (e), 21.4 (e), 22.8 (e), 24.7 (e), 27.3 (e), 28.5 (e), 28.8 (e), 29.3 (e) 67.1 (e), 81.3 (e), 89.5 (e), 110.3 (e), 123.8 (e), 127.6 (o), 128.2 (o), 128.3 (o), 131.2 (o), 131.5 (o), 132.1 (o), 137.7 (o), 137.9 (o), 140.9 (e), 146.3 (e); MS (CI, isobutane) *m*/*z* 599 isotope cluster ($MH^+ - C_3H_6$).

Macrocyclic *o*-Stannyl Sulfone 19.[12] An NMR tube solution containing **15** (15.3 mg, 24 μmol), tributyltin hydride (7.7 μL, 29 μmol), and AIBN (4 mg, 24 μmol) in benzene-d_6 (1.2 mL) was deoxygenated by the freeze−pump−thaw method and then heated to reflux. (An NMR tube was again employed as the reaction vessel to facilitate observation of the reaction.) After 5.5 h at 80 °C, the clear, colorless reaction mixture was concentrated in vacuo and the residue purified by flash chromatography on silica gel using 5% ethyl acetate in hexane as the eluent to afford 12.4 mg (86% yield) of **19**: white crystals (recrystallized from hexane to provide the X-ray sample), mp 115−119 °C; ^{1}H NMR (C_6D_6) δ 0.40−0.50 (m, 1H), 0.66 (t, J = 7.3, 3H), 0.67−1.53 (m, 20H), 1.54−1.84 (m, 6H), 2.19−2.62 (m, 4H), 7.01 (t, J = 7.4, 1H), 7.10 (d, J = 7.4, 2H), 7.22 (t, J = 7.4, 2H), 7.41 (s, 1H), 7.53 (d, J = 7.5, 2H), 7.72 (d, J = 7.5, 1H), 7.98 (d, J = 7.5, 1H); ^{13}C NMR ($CDCl_3$) δ 12.2 (e), 13.4 (o), 13.7 (o), 17.1 (e), 20.2 (e), 21.7 (e), 21.9 (e), 25.0 (e), 26.1 (e), 26.6 (e), 27.6 (e), 28.4 (e), 28.5 (e), 28.9 (e, 2 carbons, not resolved), 41.0 (e), 69.1 (e), 126.8 (o), 127.8 (o), 128.1 (o, 2 carbons, not resolved), 128.7 (o, 2 carbons, not resolved), 131.5 (o), 132.5 (o), 137.4 (o), 140.9 (e), 142.3 (o), 145.4 (e), 148.1 (e), 149.3 (e); MS (CI, isobutane) *m*/*z* 601 isotope cluster (MH^+).

(12) The author has deposited atomic coordinates for compound **19** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, U.K.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of new compounds described in the text (21 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. X-ray structural information relating to compound **19** can be obtained from the Cambridge Crystallographic Data Centre.

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