Diverging Effects of Steric Congestion on the Reaction of Tributylstannyl Radicals with Areneselenols and Aryl Bromides and Their Mechanistic Implications

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Received December 28, 1998

The effects of bulky ortho,ortho′ groups on the reactions of aryl bromides and areneselenols with tributylstannane have been studied. Bulky ortho,ortho′ groups accelerate the reaction of the bromides with the stannane but retard the reactions of the selenols. On the other hand, ab initio and force field calculations show that introducing bulky ortho substituents into selenols causes a greater increase in strain than in the corresponding bromides. Two possible explanations for the divergent reactivity patterns are advanced. On one hand, it is possible that bromine abstraction by stannyl radicals from aryl bromides proceeds in a single step through a linear transition state whereas the abstraction of SeH from the selenols involves a T-shaped, hypervalent intermediate. Alternatively, it may be that both reactions are concerted with the bromine abstraction having a late transition state and the SeH abstraction an early one. Approximate second-order rate constants for the reaction of tributylstannane with a range of hindered aryl bromides are derived from competition reactions. 2,4,6-Tri-*tert*-butylbenzeneselenol is able to function moderately well as a catalyst for the stannane-mediated reactions of vinyl bromides. The X-ray crystal structure of bis-(2,4,6-triisopropylphenyl) diselenide is presented.

Introduction

For several years now we have been studying the catalytic effect of diphenyl diselenide (**1**) on the reactions of alkyl and aryl halides with stannanes.[1−6] The effect, which parallels Roberts' catalysis of silane-mediated reductions by thiols,[7] arises because of the in situ reduction of the diselenide to the selenol according to eq 1,

$$R_3SnH + PhSeSePh \rightarrow R_3SnSePh + PhSeH \quad (1)$$

the subsequent participation of the selenol in the chain sequence of eqs 2−4, and the 1000-fold difference in the rate of trapping of alkyl radicals by PhSeH and Bu_3SnH.[8,9]

$$R^{\bullet} + PhSeH \rightarrow RH + PhSe^{\bullet} \quad (2)$$

$$PhSe^{\bullet} + Bu_3SnH \rightarrow PhSeH + Bu_3Sn^{\bullet} \quad (3)$$

$$Bu_3Sn^{\bullet} + RX \rightarrow Bu_3SnX + R^{\bullet} \quad (4)$$

The catalytic effect of the selenol on the quenching of aryl radicals by stannanes, on the other hand, is much smaller as the rate constant for their direct reaction with stannanes (eq 5) already approaches the diffusion controlled limit.[10]

$$Ar^{\bullet} + Bu_3SnH \rightarrow ArH + Bu_3Sn^{\bullet} \quad (5)$$

This difference in catalytic efficiency means that aryl radical cyclizations are not significantly inhibited by the presence of catalytic PhSeH (**4**) while alkyl radical rearrangements may be effectively prevented under the same conditions. Thus, the catalytic selenol method can be used to significantly improve the 5-exo/6-endo ratios of aryl and vinyl radical cyclizations[1,3] by preventing the rearrangement of the kinetic 5-exo closed alkyl radical,[11,12] with no appreciable loss of overall yield. In practice, this sequence is effective when aryl or vinyl iodides are used as radical precursors but fails with the corresponding aryl or vinyl bromides.[1,3] This discrepancy arises because the catalytic species, PhSeH, itself is cleaved by stannanes more easily than aryl bromides and so is rapidly destroyed, whereas aryl iodides, with the weaker aryl−halogen bond, react more rapidly with the stannane, permitting the selenol to persist until all of the iodide has been consumed. We therefore began a study aimed at the design and synthesis of selenols more resistant to cleavage by stannanes, which in turn would enable the extension of the catalytic chemistry to the more readily available aryl and vinyl bromides. In the course of this project we had occasion to investigate the effects of steric congestion on the reaction of stannyl radicals with both areneselenols and aryl bromides. This

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10.1021/jo982514a CCC: $18.00
Published on Web 03/30/1999

Table 1. ^{77}Se NMR Chemical Shifts

entry	compd	δ^a	lit. δ^a
1	**1**	460	460[2,20]
2	**2**	360.6	359;[20] 569[b,18]
3	**3**	515.7	515;[20] 516;[19] 521[b,21]
4	**4**	142.1	142.2[2]
5	**5**	−9.6	9.8[b,18]
6	**6**	119.1	24.8[b,18]
7	**7**	−26.8	−27.7[2]
8	**8**	−198.1	
9	**9**	−19.5	

[a] Unless otherwise stated all chemicals shifts are for C_6D_6 solutions referenced to external Me_2Se. [b] $CDCl_3$ solution referenced to Me_2Se.

led to the surprising discovery that bulky ortho substituents actually accelerate the cleavage of the bromides,[13,14] whereas, as anticipated, they retard that of the selenols. We now present in full the results of this investigation together with the mechanistic implications of the divergent effects of steric congestion on the two reactions, which are relevant to the current widespread interest in homolytic substitutions.[15−17]

Results and Discussion

We began by investigating the reaction of tributyltin hydride with bis(2,4,6-tri-*iso*-propyl)phenyl diselenide (**2**)[18] and bis(2,4,6-tri-*tert*-butyl)phenyl diselenide (**3**).[19] As described previously,[2] a C_6D_6 solution of **1** (0.32 M) was treated under Ar at room temperature with 1.1 equiv of Bu_3SnH resulting in rapid decolorization and the formation of two new peaks in the ^{77}Se NMR spectrum at δ 142.1 and −26.8 (Table 1). These chemical shifts agreed

Ar−Se−Se−Ar

1: Ar = Ph
2: Ar = C_6H_2-2,4,6-(i-Pr)$_3$
3: Ar = C_6H_2-2,4,6-(t-Bu)$_3$

Ar−SeH

4: Ar = Ph
5: Ar = C_6H_2-2,4,6-(i-Pr)$_3$
6: Ar = C_6H_2-2,4,6-(t-Bu)$_3$

Ar−Se−$SnBu_3$

7: Ar = Ph
8: Ar = C_6H_2-2,4,6-(i-Pr)$_3$
9: Ar = C_6H_2-2,4,6-(t-Bu)$_3$

PhSe−SeC_6H_2-2,4,6-(t-Bu)$_3$

10

well with values previously observed in this laboratory and were assigned to **4** and **7**, respectively. When 2.2 equiv of Bu_3SnH was used, only the signal at δ −26.8 was observed, which indicates that PhSeH is indeed rapidly cleaved by excess Bu_3SnH. In the case of reduction of **2** with 1.1 equiv of Bu_3SnH, signals were observed at δ −9.6 and −198.1, which, as the former disappeared on treatment with further Bu_3SnH, were assigned as **5** and **8**, respectively. With **3**, decolorization was noticeably slower, indicating that steric hindrance was certainly retarding attack of the stannane on the diselenide. Nevertheless, **3** was cleanly converted to two new signals at δ 119.1 and −19.5 in the ^{77}Se NMR spectrum over the course of the acquisition. Addition of 1 equiv of Bu_3SnH did not result in loss of either signal over a period of several hours at room temperature. However, brief heating of **3** with 2.2 equiv of Bu_3SnH to 80 °C in C_6D_6 followed by inspection by ^{77}Se NMR revealed that the signal at δ 119.1 was lost under these conditions.

Thus, it appears clear that all three diselenides (**1**−**3**) react stoichiometrically with Bu_3SnH according to eq 1 and that the selenols **4** and **5** are decomposed significantly more rapidly by further stannane than the more hindered **6**, which, nevertheless, reacts further on brief heating with Bu_3SnH.

Unfortunately, the above experiments are not quantitative, and the acquisition times required, typically several hours at the concentrations employed, for the ^{77}Se NMR experiments effectively preclude the use of this method for the determination of kinetics. Equally unfortunately, monitoring of reaction mixtures by GC was unsatisfactory owing to the very long retention times and/or decomposition of the tin selenides (**7**−**9**). Thus, we turned to competition experiments in order to glean some information on the relative rates of **1**−**3** and of **4**−**6** with Bu_3SnH. A 1:1 mixture of **1** and **3** was allowed to react with 1 equiv of Bu_3SnH when the ^{77}Se NMR spectrum revealed signals corresponding to the two diselenides (**1** and **3**), one selenol (**6**), and one stannyl selenide (**7**). With 2.2 equiv of stannane, the only two signals in the ^{77}Se NMR were those of **6** and **7**. These observations are best interpreted in terms of rapid reduction of the less hindered diselenide (**1**) according to eq 1, followed by attack of PhSeH (**4**) or PhSe$^\bullet$ on the more hindered diselenide (**3**) with formation of a mixed diselenide (**10**) and selenol (**6**) or the corresponding selenyl radical. The lack of any signals corresponding to **10** in the NMR spectrum evidently requires it to further react with PhSeH or PhSe$^\bullet$ to give the symmetrical **1** and **6** or the corresponding selenyl radical. Evidently, an equilibration is taking place that is driven by the release of the steric strain inherent in the hindered diselenides **3** and **10**. This equilibration effectively excludes any possibility of accessing relative rate data by this type of competition experiment. An alternative mechanism for equilibration involving reaction of Bu_3SnH with **10** is considered less likely as this would require the contrasteric attack of the stannane on the more hindered of the two selenium atoms.

Based on the, in retrospect, naive assumption that steric hindrance would affect aryl bromides and arene selenols in the same way, we therefore turned to the reaction of a series of aryl bromides with stannanes. These reactions, giving Bu_3SnBr as byproduct, could be monitored readily by GC. Preliminary experiments in which bromobenzene and 2,4,6-tri-*tert*-butylbromobenzene were allowed to compete for reaction with tributylstannane revealed the initial assumption to be flawed, with the more hindered bromide reacting more quickly. Following this preliminary observation, we conducted a series of competition reactions in order to determine the relative rates of reductive debromination of the aryl bromides **11**−**16** and of decyl bromide (**18**). 2-Bromoacetophenone (**15**) and decyl bromide (**18**) were included in

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Table 2. Approximate Relative and Absolute Rates for Bromine Abstraction by $Bu_3Sn^•$ at 80 °C

entry	bromide	k_{rel}	k (M^{-1} s^{-1})
1	pentafluorobromobenzene (**11**)	>50	$>1 \times 10^8$
2	1-bromodecane (**18**)	15.2	5.8×10^7
3	2,4,6-triphenylbromobenzene (**12**)	15.2	5.8×10^7
4	2,4,6-tri-*tert*-butylbromobenzene (**13**)	9.5	2.9×10^7
5	2-acetylbromobenzene (**15**)	6.7	1.6×10^7
6	2-phenylbromobenzene (**16**)	2.6	6.2×10^6
7	2,4,6-tri-*iso*-propylbromobenzene (**14**)	2.6	6.2×10^6
8	4-*tert*-butylbromobenzene (**17**)[a]	1	2.4×10^6

[a] Taken from Curran.[22]

Ar—Br

11: Ar = C_6F_5
12: Ar = C_6H_2-2,4,6-Ph
13: Ar = C_6H_2-2,4,6-(t-Bu)$_3$
14: Ar = C_6H_2-2,4,6-(i-Pr)$_3$
15: Ar = C_6H_4-2-COMe
16: Ar = C_6H_4-2-Ph
17: Ar = C_6H_4-4-t-Bu

n-$C_{10}H_{21}$—Br

18

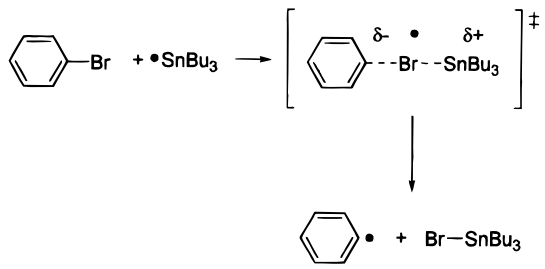
this series in order for us to be able to overlap and interface with a similar series of aryl bromides previously reported by Curran.[22] Furthermore, Curran deduced, from the known activation energy and rate constant at 25 °C, the rate constant for abstraction of bromine from a primary alkyl bromide by tributyltin radicals at 80 °C to be 5.8×10^7 M^{-1} s^{-1}. This therefore enables the relative rate data from the competition experiments to be converted into the approximate absolute values given in Table 2.

In his earlier study using a wider range of nonhindering, electron-withdrawing and -donating substituents Curran concluded that the transition state for bromine abstraction from aryl bromides by the tributylstannyl radical is slightly polarized with a partial negative charge located on the σ framework of the arene (Scheme 1).[22] We see no reason to disagree with this general conclusion and simply highlight the anomalies of entries 4 and 7 in Table 2.

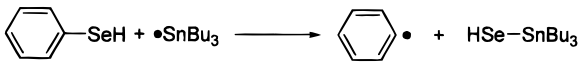
In effect, bromides **13** and **14** with their electron-donating substituents are out of the expected sequence. We attribute these exceptions to the sterically bulky nature of the isopropyl and *tert*-butyl groups and acceleration due to the relief of steric strain. Examples of such steric acceleration of bimolecular radical reactions[23,24] are much less common than their unimolecular counterparts.[25] A closely related example of the same phenomenon was reported recently, however, in which bromine abstraction from 3-bromodurene was accelerated by the butressing effect of the methyl groups.[14]

We also note the very high rate constant for reaction of pentafluorobromobenzene (**11**) with tributylstannyl radicals (Table 2, entry 1). With a lower limit of 10^8 M^{-1} s^{-1} this must qualify as one of the most rapid bromine abstractions known. Certainly, it is comparable to the rates of halogen abstraction from alkyl bromides and aryl iodides, if not with the perfluoroalkyl bromides.[26] The extreme reactivity of **11** possibly stems from the strongly

Scheme 1



Scheme 2



electron-withdrawing effect of the combined fluorine atoms stabilizing the polarized transition state, but we cannot rule out an electron-transfer mechanism in this case. 2,4,6-Triphenylbromobenzene (**12**) also showed enhanced reactivity in its reaction with stannyl radicals (Table 2, entry 3). This may be attributed to the combination of three factors: (i) the stabilization of the polar transition state by the three phenyl groups, (ii) relief of steric strain, and (iii) relief of steric inhibition of resonance. However, as with **11**, we cannot rule out a single electron-transfer mechanism in this case.

We had anticipated that areneselenols would react with stannyl radicals by a process involving SeH abstraction giving an aryl radical, analogously to the situation with the bromides. However, the differing effect of sterically bulky ortho groups in the two cases, accelerating the one and decelerating the other, caused us to bring this assumption into question. For example, ipso attack of the stannyl radical on the selenol with formation of Bu_3SnPh and $HSe^•$ was now entertained as a possible alternative mechanism for the selenols. To differentiate between the two possibilities, diselenide **2** was exposed under Ar to 1.25 equiv of Bu_3SnH in benzene resulting in complete decolorization within 15 min at room temperature. A further 1.25 equiv of Bu_3SnH was then added and the solution refluxed for 1 h, after which time GC analysis of the reaction showed the formation of triisopropylbenzene in 95% yield. Thus, one of the two aryl groups of the diselenide is cleanly converted to the arene on addition of the second portion of Bu_3SnH. This is in accord with an overall reaction scheme (Scheme 2) in which the selenol reacts with the stannane analogously to the bromide.

The X-ray crystal structure of 2,4,6-triphenylbromobenzene (**12**) shows it to be a perfectly normal aryl bromide with the bromine atom fully in the plane of the central arene ring.[27] Similarly, the structure of 2,4,6-tri-*tert*-butylbromobenzene (**13**), as contained within a crystal structure of {Li(n-Bu)}$_2$(LiMes*)$_2$·Mes*Br (where Mes* is tri-*tert*-butylphenyl) appears perfectly normal.[28] With both **12** and **13** the C—Br bond length is typical for an aryl bromide (Table 3). X-ray data are not available for the selenols, but the structure of diphenyl diselenide (**1**) has been previously determined.[29] Bis(2,4,6-triisopropyl)-phenyl diselenide (**2**) gave crystals suitable for X-ray

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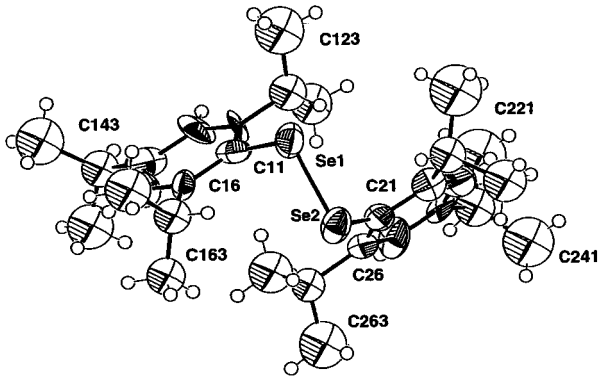

Figure 1. ORTEP drawing of the molecular structure of **2** showing the full molecule with thermal ellipsoids at the 50% probability level. Numbering of atoms within the phenyl rings proceeds according to the scheme C(*x*1)···C(*x*6) according to the pattern shown. Isopropyl carbons are numbered with the C(*xy*1)···C(*xy*3) pattern.

Table 3. Observed and Calculated Ar−X Bond Lengths (Å)

Ar	Ar−SeSeAr (obsd)	Ar−SeH (calcd) STO-3G/MM	Ar−Br (obsd)
Ph	1.93[29]	1.93/1.93	1.85[32]
2,4,6-tri-*iso*-propyl-Ph	1.86	1.93/1.95	
2,4,6-tri-*tert*-butyl-Ph		1.93/1.94	1.87[28]
2,4,6-triphenyl-Ph			1.89[27]

diffraction from pentane. Its structure was subsequently revealed to be perfectly normal (Figure 1) even though the C−Se bond length was somewhat shorter than in **1**. Unfortunately, crystals of **3** suitable for diffraction could not be obtained. To probe the selenols themselves we turned to computational methods. Ab initio calculations at the STO-3G level and molecular mechanics calculations using the universal force field were conducted (Table 3). Both methods revealed the C−Se bond length to be the same as in diselenide **1** and unaffected by substitution in the ortho position.[30] A plot of total energy, as determined by molecular mechanics calculations, in a series of increasingly hindered 2,6-disubstituted aryl bromides against the same function for the comparable selenols (Figure 2)[31] reveals that strain increases more severely in the selenols than in the bromides. This appears to be a function of the Se−H bond by virtue of which the SeH group is significantly larger than a bromine atom. Both the ab initio and molecular mechanics calculations show the C−Se−H bond angle to be 94 ± 4°, somewhat smaller than the C−Se−Se bond angle found crystallographically in **1**[29] and **2**. The dihedral angle C−C−Se−H increases from 0°, in the case of the unsubstituted selenol **1** through 45° in selenol **5** to 89° in **6**. This change in dihedral angle is related to that seen crystallographically in the diselenides; in **1** the C−C−Se−Se angle is ∼0°, whereas in **2** it is 76°. Clearly, the rotation about the C−Se bond reduces steric strain but does so at the cost of reduced orbital overlap.

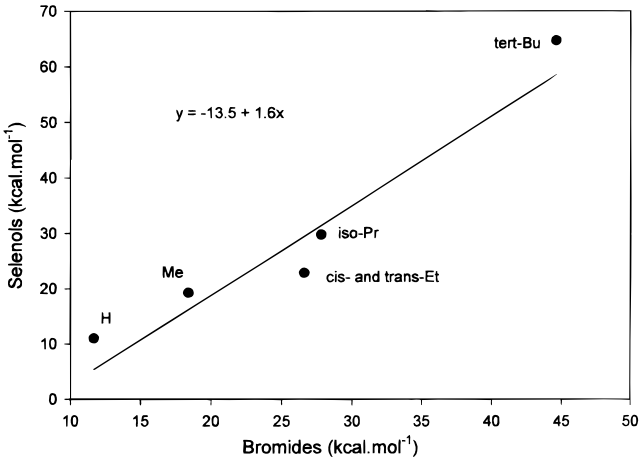

Figure 2. Total energy of 2,6-disubstituted selenols vs bromides.[31]

The greater increase in strain with substitution found in the selenols, as compared to the bromides, coupled with the absence of unusual structural features in either case, is at apparent odds with the differing effects of ortho substitution on the reactions of the two series with tributyltin hydride. We suggest that this dichotomy can best be reconciled through the operation of different mechanisms in the two series. The most recent high-level ab initio calculations by the Schiesser group on homolytic substitution at bromine and selenium indicate that these reactions proceed smoothly in a single step via essentially linear transition states, as opposed to via hypervalent intermediates, at least for the simple systems studied. Thus, Schiesser found computationally that hydrogen atoms abstract Br from HBr and MeBr via linear transition states.[33] Similarly, $Me^{\bullet}$ and $H_3Sn^{\bullet}$ both were calculated to react with MeBr via backside attack on the bromine without the intervention of any intermediates.[33] Comparable calculations also indicated that the reaction of both $Me^{\bullet}$ and $H_3Sn^{\bullet}$ on MeSeH takes place via backside attack leading to T-shaped transition states, not hypervalent intermediates.[34] At the highest levels of theory used $SeH_3^{\bullet}$ was also found to be a T-shaped transition state.[35] The results obtained here are most consistent with the tributylstannyl radicals abstracting bromine from the aryl bromides in a single step, as shown in Scheme 1, with a lengthening of the C−Br bond and a concomitant reduction in strain at the transition state. On the other hand, the retarding effect of increasing steric bulk on the reaction of the stannyl radicals with the selenols is most consistent with a stepwise process involving reversible formation of a T-shaped intermediate selenanyl radical that shows increased strain over and above the ground-state selenol (Scheme 3). This is not to say that the calculations of Schiesser et al. are incorrect for the simple reactions studied, only that substituents can have a significant effect on the mechanism of the homolytic substitution especially when capable of stabilizing a hypervalent intermediate. Alternatively, it may be that both sets of reactions proceed along concerted

(30) Dynamic NMR of hindered diselenides: Pinto, B. M.; Leung, R. Y. N.; Sharma, R. D. *Magn. Reson. Chem.* **1988**, *26*, 729−734.

(31) The relationship indicated in Figure 2 is not intended to suggest any linear correlation, but simply to help convey the idea of the differing effects of strain on the two classes of molecule. A similar plot is obtained using the energies obtained from the MO calculations.

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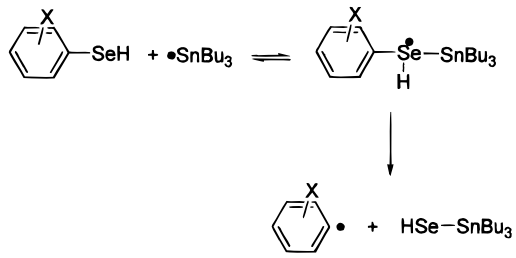
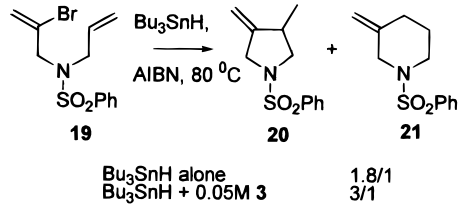
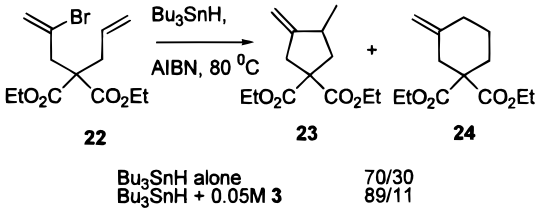
Scheme 3



Scheme 4



Scheme 5



pathways with backside attack but with transition states located at different points on the reaction coordinate. Thus, the Br abstraction could be taking place via a late transition state with a long C−Br bond, resulting in the observed steric acceleration, whereas the transition state for SeH abstraction may be early, with a short C−Se bond, leading to steric hindrance of the approach of the stannyl radical. However, the computations of Schiesser mitigate against this possibility.[33,34] At the highest level of theory employed (QCISD/MP2) these authors find the abstraction of Br from MeBr by $H_3Sn^•$ to be substantially exothermic, i.e., with an early transition state, whereas that of SeH from MeSeH by $H_3Sn^•$ is marginally endothermic, i.e., with a later transition state.[33,34] Although these calculations are for abstractions from sp^3 C−X bonds, and not the sp^2 C−X bonds studied here, it is reasonable to suppose that the trend will be similar.

Finally, returning to the initial objective, we briefly investigated the ability of the hindered selenol **6**, introduced as **3**, to inhibit radical rearrangements in reactions in which the original radical is derived from sp^2 C−Br bonds. Thus, a refluxing 0.05 M benzene solution of vinyl bromide **19** was treated dropwise with Bu_3SnH and catalytic AIBN over 3 h, which resulted in the formation of the kinetic and thermodynamic products **20** and **21** in the ratio of 1.8/1. When the reaction was repeated in the presence of 10 mol % **3**, i.e., 0.005 M **6**, the ratio was 3/1 (Scheme 4). In a similar experiment, vinyl bromide **22** gave a ratio of **23**/**24** = 7/3 without the catalyst and 89/11 in the presence of 0.005 M **6** (Scheme 5). Thus, it is seen that although **6** is eventually destroyed by Bu_3SnH in benzene at reflux, reaction of the stannane with the bromide is competitive and catalysis can be achieved. Work is in progress on the further development of stable selenol catalysts and will be reported in due course.

Table 4. Selected Bond Distances, Angles, and Torsional Angles for 2

atoms	distance	atoms	distance
Se1−Se2	2.336(3)	Se2−C21	1.87(2)
Se1−C11	1.86(2)	C21−C22	1.40(3)
C11−C12	1.36(3)	C21−C26	1.47(4)
C11−C16	1.43(3)	C22−C23	1.35(4)
C12−C13	1.38(3)	C23−C24	1.42(4)
C13−C14	1.44(3)	C24−C25	1.30(3)
C14−C15	1.37(4)	C25−C26	1.37(4)
C15−C16	1.37(3)		

atoms	angle	atoms	angle
Se2−Se1−C11	101.5(6)	Se1−Se2−C21	100.1(7)
Se1−C11−C12	121(2)	Se2−C21−C22	123(2)
Se1−C11−C16	120(2)	Se2−C21−C26	121(2)

atoms	angle
C11−Se1−Se2−C21	76(1)
Se2−Se1−C11−C12	−108(2)
Se2−Se1−C11−C16	76(2)
Se1−Se2−C21−C22	75(2)
Se1−Se2−C21−C26	−104(2)

Experimental Section

General Procedures.[36] Bis(2,4,6-tri-*iso*-propyl)phenyl diselenide (**2**)[18] and bis(2,4,6-tri-*tert*-butyl)phenyl diselenide (**3**)[19] were prepared according to literature methods. The aryl bromides with the exceptions of 2,4,6-tri-*iso*-propylbromobenzene (**14**)[37] and 2,4,6-triphenylbromobenzene (**12**),[38] which were prepared according to literature methods, were commercial and used as purchased. *N*-(2-Bromo-2-propenyl)-*N*-(2-propenyl)benzenesulfonamide (**19**)[39] and diethyl 2-(2-bromo-2-propenyl)-2-(2-propenyl)-propanedioate (**22**)[40] were prepared according to the literature.

Reaction of Diselenides with Bu_3SnH with Monitoring by NMR Spectroscopy. The diselenide **1**, **2**, or **3** (0.032 mmol) was dissolved in C_6D_6 (1 mL) under Ar in a 5 mm NMR tube, and then Bu_3SnH (9.2 μL, 0.035 mmol) was added. After decolorization of the yellow solution, the ^{77}Se NMR spectrum was measured. In a second set of experiments, Bu_3SnH (18.4 μL, 0.07 mmol) was added to a solution of diselenide (0.032 mmol) and then the ^{77}Se NMR spectrum was recorded.

In a competition experiment, **1** (0.032 mmol) and **3** (0.032 mmol) were dissolved in C_6D_6 (1 mL) under Ar in a 5 mm NMR tube and then Bu_3SnH (9.2 μL, 0.035 mmol) or Bu_3SnH (18.4 μL, 0.07 mmol) was added. After standing at room temperature for 3 h, the ^{77}Se NMR spectrum was measured. A similar experiment was conducted with **1** (0.032 mmol) and **2** (0.032 mmol) and Bu_3SnH (18.4 μL, 0.07 mmol) and the ^{77}Se NMR spectrum was measured.

Competition of Bromides for Reaction with Tributyltin Hydride. To a solution of the competing bromides (0.5−1 M in dry benzene) in the ratios reported in the Supporting Information were added Bu_3SnH (0.5 equiv based on the sum of the two substrates) and a catalytic amount of AIBN. The solution was heated at 80 °C for 3 h under an inert atmosphere and cooled to room temperature, and *p*-diethoxybenzene was then added as standard and an aliquot of the solution was used for GC and NMR analysis. The relative rate constants were determined using the following equation for competitive bimolecular reactions.[22,41]

(36) For general experimental details see ref 1.
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$$k_1/k_2 = (\ln([Ar^1Br]_i/([Ar^1Br]_i - [Ar^1H])))/(\ln([Ar^2Br]_i/([Ar^2Br]_i - [Ar^2H])))$$

In almost all cases the amounts of the two residual competing substrates were determined. In a few cases it was experimentally more convenient to determine the products. The full set of experimental data is given in the Supporting Information.

Reaction of Diselenide 2 with Tributylstannane: Formation of Triisopropylbenzene. Bu_3SnH (72.7 mg, 0.25 mmol) and **2** (0.2 mmol) were dissolved in benzene (3 mL) under Ar. The solution became colorless after being stirred at room temperature for 15 min. There was no visible change in the solution after it was refluxed for 1 h under Ar, a further portion of Bu_3SnH (0.25 mmol) was then added, and the solution was refluxed for another hour after which GC analysis showed the formation of 1,3,5-triisopropylbenzene in 95% yield (i.e., one, not both, of the two arene rings), as determined with the aid of 1,3,5-tri-*tert*-butylbenzene as an internal standard.

X-ray Crystallographic Structure Determination of Bis(2,4,6-triisopropyl)phenyl Diselenide (2). Details of data collection and the results of structure refinement are given in the Supporting Information. Important bond distance and angle information is given in Table 4. Data were collected using a Mo X-ray source. An analytical absorption correction was applied to the data. Data were processed, and the structure was solved and refined on *F* using the XTAL 3.5[42,43] suite of programs. The selenium atoms and the carbon atoms in the aromatic ring were refined with anisotropic thermal parameters. Isopropyl group carbons were refined with isotropic thermal parameters. Hydrogen atoms were located in idealized positions based on the carbon backbone and were given a fixed isotropic thermal parameter $U = 0.120$. Analysis of the final Fourier difference revealed the presence of significant electron density in the vicinity of the selenium atoms and near the isopropyl group carbons. Other methods for absorption correction (Ψ scans) and inclusion of anistropic thermal parameters for the isopropyl group carbons did not remove these peaks.

Computations. Force field calculations were carried out with the Universal Force Field.[44] Ab initio calculations were carried out by the HF SCF method using the STO 3G basis set in Gaussian94. All computations were conducted with an SGI Octane system using the Cerius^2 3.0 suite of programs.

***N*-(2-Bromo-2-propenyl)-*N*-(2-propenyl)benzenesulfonamide (19):**[39] ^{1}H NMR δ 3.85 (2H, t, $J = 6.5$ Hz), 4.04 (2H, s), 5.15 (2H, m), 5.50−5.65 (2H, m), 5.83 (1H, q, $J = 1.7$ Hz), 7.48−7.60 (3H, m), 7.84 (2H, m); ^{13}C NMR δ 49.9, 53.7, 119.4, 120.0, 127.2 (2C), 127.7, 129.0 (2C), 131.7, 132.7, 140.0.

Reaction of *N*-(2-Bromo-2-propenyl)-*N*-(2-propenyl)-benzenesulfonamide (19) with Bu_3SnH and Diselenide 6: *N*-(Phenylsulfonyl)-3-methyl-4-methylenepyrrolidine (20) and *N*-(Phenylsulfonyl)-3-methylenepiperidine (21). To a 0.05 M solution of **19** (102 mg, 0.32 mmol) in benzene (3.2 mL) at reflux under Ar was added, by means of a syringe pump, a solution of Bu_3SnH (192 μL, 0.7 mmol) and AIBN (3 mg, 0.02 mmol) in benzene (3.2 mL) dropwise over 3 h. After a further 0.5 h at reflux, the reaction mixture was cooled to room temperature and the solvent removed under reduced pressure. The crude mixture was taken up in acetonitrile, washed with petroleum ether, and evaporated to give a mixture of **20** and **21** in the ratio of 1.8 and 1 as assigned by ^{1}H NMR spectroscopy. The experiment was repeated with 10 mol % of **6** added to the initial benzene solution of **19** when the ratio of **20** and **21** was found to be 3:1. **20**:[39] ^{1}H NMR δ 1.02 (3H, d $J = 6.5$ Hz), 2.55−2.74 (2H, m), 3.58 (1H, t, $J = 6.5$ Hz), 3.76 (1H, m), 3.95 (1H, m), 4.81−4.89 (2H, m), 7.44−7.62 (3H, m), and 7.80 (2H, m). **21**:[39] ^{1}H NMR δ 1.64−1.69 (2H, m), 2.08 (2H, t $J = 6.1$ Hz), 3.07 (2H, t $J = 5.6$ Hz), 3.50 (2H, s), 4.80−4.89 (2H, m), 7.44−7.62 (3H, m), and 7.80 (2H, m).

Diethyl 2-(2-bromo-2-propenyl)-2-(2-propenyl)-propanedioate (22):[40] ^{1}H NMR δ 1.24 (6H, t, $J = 7.1$ Hz), 2.76 (2H, d, $J = 7.4$ Hz), 3.13 (2H, s), 4.19 (4H, m), 5.10 (2H, m), 5.57−5.69 (3H, m); ^{13}C NMR δ 13.7 (2C), 35.9, 42.8, 56.7, 61.5 (2C), 119.5, 121.9, 127.1, 130.0, 170.0.

Reaction of Diethyl 2-(2-Bromo-2-propenyl)-2-(2-propenyl)-propanedioate (22) with Bu_3SnH and Diselenide 6: 4,4-Bis(ethoxycarbonyl)-1-methyl-2-methylenecyclopentane (23) and 1,1-Bis(ethoxycarbonyl)-3-methylenecyclohexane (24). To a 0.05 M solution of **22** (104 mg, 0.31 mmol) in benzene (3.2 mL) at reflux under Ar was added, by means of a syringe pump, a solution of Bu_3SnH (192 μL, 0.7 mmol) and AIBN (3 mg, 0.02 mmol) in benzene (3.2 mL) dropwise over 3 h. After a further 0.5 h at reflux, the reaction mixture was cooled to room temperature and the solvent removed under reduced pressure. The crude product mixture was taken up in acetonitrile, washed with petroleum ether, and evaporated to give a mixture of **23** and **24** in a ratio of 70:30 as assigned by ^{1}H NMR spectroscopy. When the experiment was conducted in the presence of 10 mol % of **6** added to the initial benzene solution of **22** the ratio of **23**:**24** was 89:11. **23**:[40] ^{1}H NMR δ 1.08 (3H, d $J = 6.3$ Hz), 1.25 (6H, dt, $J = 1.1$, 7.0 Hz), 1.71 (1H, m), 2.58 (2H, m), 3.0 (2H, q, $J = 17.0$ Hz), 4.18 (4H, m), 4.79 (1H, d, $J = 2.1$ Hz), 4.89 (1H, d, $J = 2.0$ Hz); ^{13}C NMR δ 13.9 (2C), 17.8, 37.2, 40.4, 42.0, 58.1, 61.3 (2C), 105.3, 153.3, 171.9 (2C). **24**:[40] ^{1}H NMR δ 1.25 (6H, t, $J = 7.1$ Hz), 1.65 (2H, m), 2.08 (4H, m), 2.65 (2H, s), 4.18 (4H, m), 4.70 (2H, s).

Acknowledgment. We are grateful to the NSF (CHE 9625256) for support of this work and to Drs. John and Cynthia Harwood for their help with multinuclear NMR spectroscopy and computations, respectively. F.R. thanks the Politecnico di Milano for study leave and support.

Supporting Information Available: Table of experimental data for the competitive reactions of aryl bromides with tributylstannane and X-ray structural data for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO982514A

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