Stannane-Mediated Radical Addition to Arenes. Generation of Cyclohexadienyl Radicals and Increased Propagation Efficiency in the Presence of Catalytic Benzeneselenol

David Crich* and Jae-Taeg Hwang

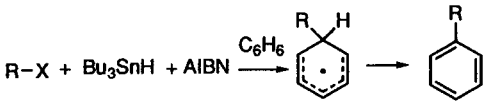
Department of Chemistry, University of Illinois at Chicago, 845 West Taylor Street, Chicago, Illinois 60607-7061

Received December 3, 1997

Introduction

In preparative free radical chemistry, the highest yielding, cleanest reactions are typically chain sequences in which each of the individual propagation steps is rapid.[1] Adherance to this paradigm enables radical concentration to be maintained at a minimum which in turn reduces the possibility of debilitating radical−radical reactions. Inefficiency in any one of the several propagation steps in a given chain sequence will lead to a build up of radical concentration, the consequent formation of dimerization and disproportionation products, and a shortening of the kinetic chain length. This latter phenomenon in turn requires the use of abnormally high amounts of chain initiator if the substrate is to be fully consumed. A case in point, and the focus of this study, is the stannane-mediated addition of radicals to arenes. Here (Scheme 1), a cyclohexadienyl radical is generated which is reluctant to propagate the chain by hydrogen abstraction from the stannane. In this chemistry the ultimate fate of the cyclohexadienyl radical is usually rearomatization to a substituted arene,[2,3] but the mechanism by which this oxidation step takes place is not at all well understood and is the subject of debate in the literature. Capture by the stannane to give regiosiomeric mixtures of cyclohexadienes which are oxidized on work up or chromatography is often assumed. However, the ease of formation and isolation of cyclohexadienes from Birch type reductions[4] of arenes belies this argument, at least as the major pathway. The poor propagation and short kinetic chain lengths of such reactions with the consequent need for disproportionately large amounts of initiator have led to the suggestion that the cyclohexadienyl radicals may be oxidized by the initiator,[5] usually AIBN, or an initiator-derived radical.

Scheme 1



Some support for this hypothesis may be drawn from the work of Engel,[6] in which it is demonstrated that benzhydryl radicals reduce azo compounds. More recent work by Rosa et al. with labeled compounds mitigates against this mechanism, at least for AIBN.[7] Bowman and coworkers have advanced a further hypothesis, related to the $S_{RN}1$ type reaction, in which the adduct radical undergoes deprotonation to give a radical anion which, in turn, transfers an electron to the alkyl halide and so achieves aromaticity.[8] As written by Bowman, this mechanism, which has found some support,[9,10] uses the stannane as a base to perform the proton abstraction leading to the formation of molecular hydrogen gas and a stannyl radical.

Others have taken advantage of the ability of cyclohexadienyl radicals to expel stabilized heteroatomic and carbon-centered radicals to design radical chain sequences leading to inter- and intramolecular ipso-substitution reactions of arenes.[11] Walton has advanced such a fragmentation as a new means of entry into carbon radicals.[12]

We have been interested in the catalysis of stannane-mediated radical chain reactions by selenols, a process which in its simplest form may be formulated as the three propagation step sequence of eqs 1−3.[13]

$$R^{\bullet} + PhSeH \rightarrow RH + PhSe^{\bullet} \quad (1)$$

$$PhSe^{\bullet} + Bu_3SnH \rightarrow PhSeH + Bu_3Sn^{\bullet} \quad (2)$$

$$Bu_3Sn^{\bullet} + RX \rightarrow Bu_3SnX + R^{\bullet} \quad (3)$$

This sequence functions because of the 1000-fold difference in rate constants for hydrogen atom abstraction from stannanes[14] and selenols[15] by alkyl radicals. Its utility is enhanced by the ability to introduce benzeneselenol as diphenyl diselenide which is reduced in situ

(1) Motherwell, W. B.; Crich, D. *Free Radical Chain Reactions in Organic Synthesis*; Academic Press: London, 1992.

(2) Beckwith, A. L. J.; Ingold, K. U. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 1, pp 162−310.

(3) For example see: (a) Estevez, J. C.; Villaverde, M. C.; Estevez, R. J.; Castedo, L. *Tetrahedron* **1995**, *51*, 4075−4082. (b) Jones, K.; Ho, T. C. T.; Wilkinson, J. *Tetrahedron Lett.* **1995**, *36*, 6743−6744. (c) Murphy, J. A.; Sherburn, M. S. *Tetrahedron* **1991**, *47*, 4077−4088. (d) Narashiman, N. S.; Aidhen, I. S. *Tetrahedron Lett.* **1988**, *29*, 2987−2988. (e) Rosa, A. M.; Lobo, A. M.; Branco, P. S.; Prabhakar, S. *Tetrahedron* **1997**, *53*, 285−298. (f) Rosa, A. M.; Lobo, A. M.; Branco, P. S.; Prabhakar, S.; Sá-da-Costa, M. *Tetrahedron* **1997**, *53*, 299−306. (g) Togo, H.; Kikuchi, O. *Tetrahedron Lett.* **1988**, *29*, 4133−4134.

(4) Birch, A. J.; Subba Rao, G. In *Advances in Organic Chemistry*; Taylor, E. C., Ed.; Wiley-Interscience: New York, 1972; Vol. 8, pp 1−65.

(5) (a) Curran, D. P.; Yu, H.; Liu, H. *Tetrahedron* **1994**, *50*, 7343−7366. (b) Curran, D. P. *J. Chem. Soc., Perkin Trans. 1* **1994**, 1377−1393.

(6) Engel, P. S.; Wu, W.-X. *J. Am. Chem. Soc.* **1989**, *111*, 1830−1835.

(7) Rosa, A. M.; Lobo, A. M.; Branco, P. S.; Prabhakar, S.; Pereira, A. M. D. L. *Tetrahedron* **1997**, *53*, 269−284.

(8) (a) Bowman, W. R.; Heaney, H.; Jordan, B. M. *Tetrahedron* **1991**, *47*, 10119−10128. (b) Aldabbagh, F.; Bowman, W. R. *Tetrahedron Lett.* **1997**, *38*, 3793−3794. (c) Aldabbagh, F.; Bowman, W. R.; Mann, E. *Tetrahedron Lett.* **1997**, *38*, 7937−7940.

(9) Moody, C. J.; Norton, C. L. *J. Chem. Soc., Perkin Trans. 1* **1997**, 2639−2643.

(10) Beckwith, A. L. J.; Storey, J. M. D. *J. Chem. Soc., Chem. Commun.* **1995**, 977−978.

(11) (a) da Mata, M. L. E. N.; Motherwell, W. B.; Ujjainwalla, F. *Tetrahedron Lett.* **1997**, *38*, 137−140. (b) da Mata, M. L. E. N.; Motherwell, W. B.; Ujjainwalla, F. *Tetrahedron Lett.* **1997**, *38*, 141−144. (c) Aboutayab, K.; Caddick, S.; Jenkins, K.; Joshi, S.; Khan, S. *Tetrahedron* **1996**, *52*, 11329−11340. (d) Giraud, L.; Lacote, E.; Renaud, P. *Helv. Chim. Acta* **1997**, *80*, 2148−2156.

(12) (a) Baguley, P. A.; Binmore, G.; Milne, A.; Walton, J. C. *J. Chem. Soc., Chem. Commun.* **1996**, 2199−2200. (b) Binmore, G.; Cardellini, L.; Walton, J. C. *J. Chem. Soc., Perkin Trans. 2* **1997**, 757−762.

(13) (a) Crich, D.; Yao, Q. *J. Org. Chem.* **1995**, *60*, 84−88. (b) Crich, D.; Jiao, X.-Y.; Yao, Q.; Harwood: J. S. *J. Org. Chem.* **1996**, *61*, 2368−2373. (c) Crich, D.; Hwang, J.-T.; Liu, H. *Tetrahedron Lett.* **1996**, *37*, 3105−3108.

S0022-3263(97)02197-X CCC: $15.00
Published on Web 03/28/1998

by the stannane (eq 4), thereby eliminating the need to handle the noxious selenol itself.[13]

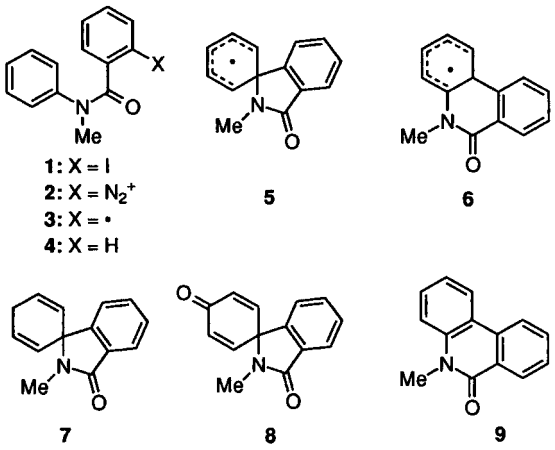
$$R_3SnH + PhSeSePh \rightarrow R_3SnSePh + PhSeH \quad (4)$$

This catalytic cycle has been found to be extremely efficient at preventing slow to moderate rearrangments of the initial alkyl radical.[13,16] More recently, we have found that benzeneselenol is also effective in promoting stannane-mediated chain reactions involving resonance stabilized allylic radicals.[17] Here, we report that benzeneselenol may also be used to catalyze the additions of aryl halides to arenes by facilitating the chain transfer step involving hydrogen atom donation to the intermediate cyclohexadienyl radicals. Moreover, the process is shown to be reductive overall and to enable the isolation of cyclohexadienes, even after extensive silica gel chromatography.

Results and Discussion

To probe our hypothesis we first selected the cyclization of iodide **1** for study. This system had previously been studied by Kharasch and,[18] subsequently, Hey when the aryl radical was generated by simple photolysis of the iodide as well as by copper-catalyzed decomposition of the corresponding diazonium salt **2**.[19] Later, it was reinvestigated by Bowman and co-workers under tin hydride-mediated conditions.[8] The initial nonchain work of the Kharasch and Hey laboratories established that the aryl radical **3** cyclizes in the 5-exo mode, giving the cyclohexadienyl radical **5**. In the absence of efficient radical traps this species undergoes rearrangement to the thermodynamic product radical **6**. Thus, operating in the presence of HI as an excellent radical trap Hey and co-workers obtained the spirocyclic cyclohexadiene **7**.[19] In the presence of oxygen the cross-conjugated ketone **8** was obtained. In the absence of efficient radical traps the phenanthridone **9** and assorted dimers of radicals **5** and **6** were obtained.[19] Working with a 10% excess of Bu_3SnH, but of unspecified concentration, in toluene at reflux with 30 mol % of AIBN, Bowman and co-workers obtained a 15% yield of **9** from iodide **1** together with 38% recovered **1**. It was stated that the low yields were due to difficulties in the removal of organotin byproducts and, importantly, that no spirocyclic products were observed in the crude reaction mixture.

First we studied the reaction of **1** with Bu_3SnH in the absence of selenol. A solution of Bu_3SnH (120 mol % vs **1**) and AIBN (15 mol % vs **1**) was added dropwise over 20 h to a 0.01 M solution of **1** in benzene at reflux under nitrogen. Chromatographic purification of the relatively complex reaction mixture enabled isolation of 37% of the recovered substrate (**1**), 23% of the reduction product (**4**), and 12% of the phenanthridone (**9**). ^1H NMR spectroscopic investigation of the crude reaction mixture indicated that the spirocyclic product (**7**) was present in only trace amounts, certainly <5% (Table 1, entry 1). These results reflect reasonably well those of Bowman and co-workers, which are characterized by the presence of large quantities of recovered substrate, indicative of poor propagation, and the isolation of the thermodynamic product **9**. Unlike Bowman, we isolated a significant quantity of the reduced substrate **4**. This, we believe, is again a function of poor chain propagation and the dropwise addition of the stannane. At the beginning of the reaction the concentration of the stannane is extremely low and, added to the poor propagating abilities of **5** and **6**, this has the effect of effectively preventing any reaction from occurring. Over time the concentration of Bu_3SnH builds up until it is sufficient to sustain the reaction but also to quench the initial aryl radical **3** before cyclization, giving **4**. This type of phenomenon is a relatively frequent, but often unrecognized, occurrence when syringe pump additions are used. Next, the experiment was repeated with the difference that diphenyl diselenide (15 mol %) was added to the initial reaction mixture. On reduction by the stannane this gives a 0.004 M solution of PhSeH. As seen from Table 1 (entry 2) this modification provoked a significant change in the course of the reaction. First, the reaction ran smoothly and all of the substrate was consumed. Second, the major product isolated was now the spirocycle **7**. Moderate amounts of the reduced substrate **4** and the phenanthridone **9** were also isolated. Thus, we conclude that benzeneselenol does catalyze the chain propagation by quenching of the kinetically cyclized radical **5**, before it undergoes rearrangement to **6**.



We next turned to **10**, the ester analogue of **1**. Dropwise addition of Bu_3SnH and AIBN to a 0.02 M solution of **10** in benzene at reflux provided the results in entry 3 of Table 1. These results, like those of entry 1, are characterized by the return of a significant amount of substrate (**10**) and formation of direct reduction product (**11**). We also isolated from this reaction mixture 5% of benzo[*c*]chromanone (**14**) and 3% of biphenyl (**15**). In the presence of 20 mol % (0.004 M) diphenyl diselenide a much smoother reaction ensued with complete conversion of the substrate. Moreover, two new, inseparable products were formed with a combined yield of 40% (Table 1, entry 4). These products were assigned structures **12** and **13** and derive from addition of the initial aryl radical to the solvent benzene followed by trapping with the

(14) At 25 °C the rate constant for hydrogen abstraction from Bu_3SnH by a primary alkyl radical is 2.4×10^6 M^{-1} s^{-1}: Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 7739−7742.

(15) At 25 °C the rate constant for hydrogen abstraction from PhSeH by a primary alkyl radical is 2.1×10^9 M^{-1} s^{-1}: Newcomb, M.; Varick, T. R.; Ha, C.; Manek, M. B.; Yue, X. *J. Am. Chem. Soc.* **1992**, *114*, 8158−8163.

(16) Newcomb, M.; Musa, O. M.; Martinez, F. N.; Horner, J. H. *J. Am. Chem. Soc.* **1997**, *119*, 4569−4577.

(17) Crich, D.; Mo, X.-S. *J. Org. Chem.* **1997**, *62*, 8624−8625.

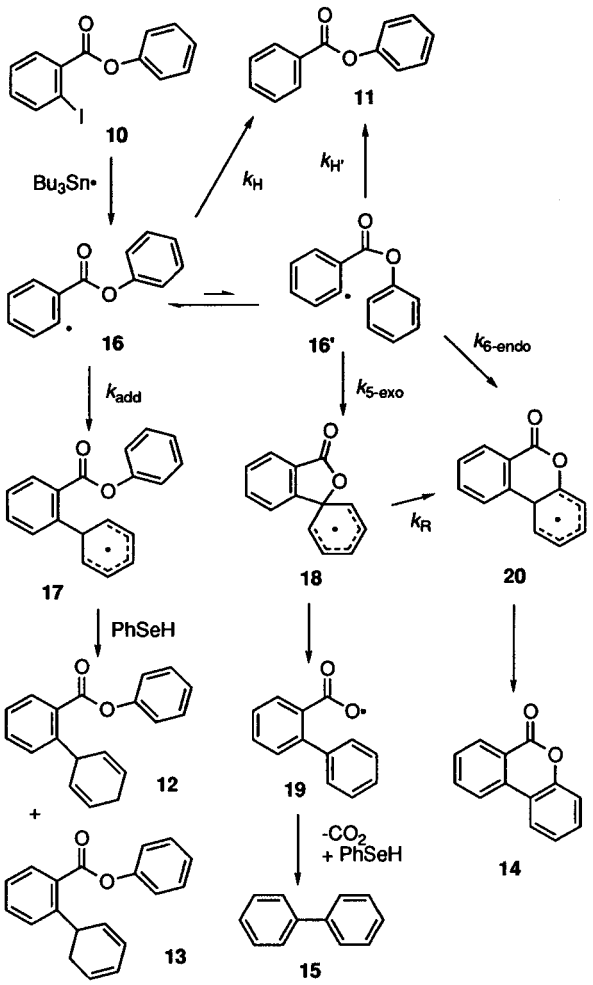
(18) Thyagarajan, B. S.; Kharasch, H. B.; Lewis, H. B.; Wolf, W. *J. Chem. Soc., Chem. Commun.* **1967**, 614−614.

(19) (a) Hey, D. H.; Jones, G. H.; Perkins, M. J. *J. Chem. Soc., Chem. Commun.* **1969**, 1375−1376. (b) Hey, D. H.; Jones, G. H.; Perkins, M. J. *J. Chem. Soc.* (C) **1971**, 116−122.

Table 1. Addition of Aryl Radicals to Arenes

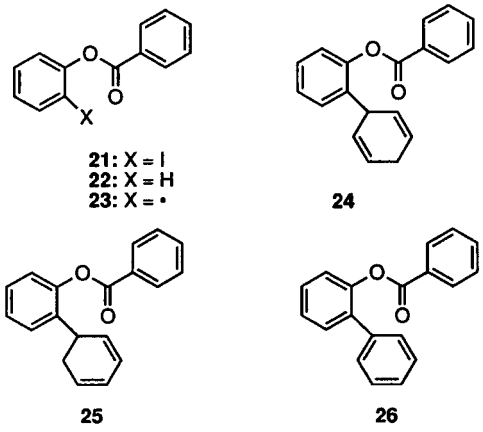
entry	substrate [conc, M]	[PhSeH] (M)%	recovered substrate	products (% yield)
1	**1** [0.01]	0	**1** (37)	**4** (23), **7** (<5), **9** (12)
2	**1** [0.01]	0.004	**1** (0)	**4** (22), **7** (43), **9** (22)
3	**10** [0.02]	0	**10** (27)	**11** (25), **14** (5), **15** (3)
4	**10** [0.02]	0.004	**10** (0)	**11** (17), **12** + **13** (40; 6.8:1) + **14** (12), **15** (21)
5	**21** [0.02]	0	**21** (32)	**22** (8), **26** (37)
6	**21** [0.02]	0.04	**21** (0)	**22** (12), **24** + **25** (77; 2.5:1), **26** (8)

Scheme 2



selenol. Inspection of the NMR spectra of the crude reaction mixtures showed that in the absence of PhSeSePh (Table 1, entry 3) these products were formed in only trace amounts. However, the same NMR spectra indicated numerous related products, which were not isolated and characterized, but which must arise from dimerization of the adduct cyclohexadienyl radical. These purported dimers, which account for much of the missing material in the uncatalyzed reactions, are more or less absent from the catalyzed process, when the mass balance is also good. We suggest that the formation of all products may be rationalized as in Scheme 2, in which it is seen that the somewhat unexpected formation of biphenyl arises from a 5-exo-trig cyclization to give **18**, with subsequent expulsion of the carboxyl radical (**19**), and eventual decarboxylation. This process is related to the biaryl synthesis developed by Motherwell.[11] The β-elimination of carboxyl radicals is a very rare process but has precedent in the work of Barton, when sufficent thermodynamic driving force, such as gain of the aromatic stabilization energy[20] or relief of ring strain,[17] is provided.

Finally, we examined **21**, the regiosiomer of **10**. In the absense of benzeneselenol (Table 1, entry 5) chain propagation was again poor and a substantial amount of substrate was recovered. The major product from this uncatalyzed reaction was the rearomatized benzene adduct **26**, which was isolated in 37% yield. In the presence of 0.004 M diphenyl diselenide, all of the substrate was consumed and the yield of **26** reduced in favor of two new products, the isomeric cyclohexadienes **24** and **25**, which were isolated in 77% combined yield (Table 1, entry 6).



The most important conclusion to be drawn from the above results is that benzeneselenol is indeed effective as a catalyst for the quenching of cyclohexadienyl radicals by stannanes. Furthermore, any cyclohexadienes soformed are relatively stable to the reaction conditions and may be isolated by silica gel chromatography without difficulty.

Selenol quenching of the various cyclohexadienyl radicals may in principle occur at either of the terminii of the pentadienyl system or at the central carbon. In practice, we observe moderate selectivity for quenching at the central carbon with preferential formation of the skipped dienes. These (**7**, **12**, and **24**) are readily discernible from their respective conjugated isomers owing to the symmetry of the 1,4-cyclohexadienyl system which is reflected in the various NMR spectra. Beckwith has previously recorded a similar phenomenon in the quenching of related cyclohexadienyl radicals by oxygen, which he attributed to the reduced steric strain in the skipped as opposed to conjugated cyclohexadiene products.[21] It seems likely that a similar effect is operative on the transition states for quenching by benzeneselenol, there being a considerable steric interaction between the incoming selenol and the adjacent substituent for quenching at the terminus of the pentadienyl system. It is possible that the use of a more bulky selenol could improve the regioselectivity of the quenching somewhat and so render the present reactions preparatively useful.

A further point of interest concerns the widely differing propensity toward cyclization or intermolecular addition

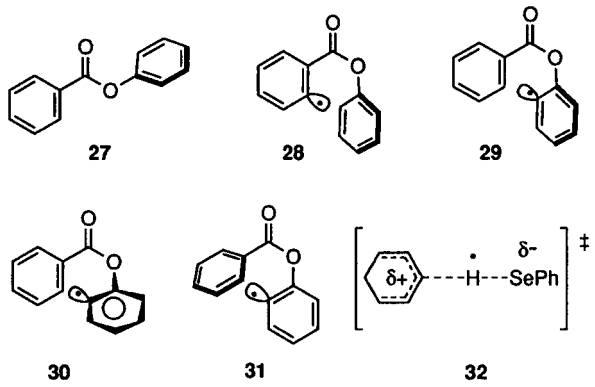
(20) Barton, D. H. R.; Dowlatshahi, H. A.; Motherwell, W. B.; Villemin, D. *J. Chem. Soc., Chem. Commun.* **1980**, 732.

(21) Beckwith, A. L. J.; O'Shea, D. M.; Roberts, D. H. *J. Am. Chem. Soc.* **1986**, *108*, 6408−6409.

to benzene of the three systems studied. With amide **1**, we found no conclusive evidence for addition to solvent. Given that the rate constant for addition of a phenyl radical to benzene is 4.5×10^5 M^{-1} s^{-1} at 25 °C[22] and taking a conservative ratio of 10:1 for the cyclization to addition products in this reaction, we estimate a minimum rate constant of 5×10^7 s^{-1} for this particular cyclization. On the other hand, with **21** no evidence for cyclization was observed. Here, taking a similarly conservative estimate of 86:2[23] for the ratio of addition to cyclization products, we estimate an absolute maximum rate constant of 1×10^5 s^{-1} for this cyclization. Somewhere between the two extremes we have the radical **16**. In this case, using a ratio of 33:40 for total cyclization to total addition derived products, we arrive at a cyclization rate constant of 4×10^6 s^{-1}. These numbers take no account of the effect of the substituents on the rate of aryl radical addition to benzene, nor of the discrepancy in temperature between the experiments described and that at which the clock reaction was measured. Nevertheless, substituent effects for the σ-type aryl radicals are relatively small,[24] and the numbers should serve as a reasonable first approximation. We also note that the numbers are for total 5-exo plus 6-endo cyclization as the present experiments do not permit us to comment on whether the 6-endo products arise directly or via rearrangment of a kinetically 5-exo cyclized radical.

The approximately 1 order of magnitude difference in cyclization rate constants between **1** and **10** can be confidently ascribed to differing rotamer populations. Unlike simple aliphatic amides, anilides and *N*-alkyl anilides are known to prefer the anti-conformation depicted.[25] Radical **3** is therefore generated in a conformation somewhat prearranged for cyclization. On the other hand, *O*-aryl esters, such as phenyl benzoate, adopt the standard syn-conformation about the C−O bond both in the crystal[26] and in solution.[27] Therefore any radical (**16**) generated from **10** will need to undergo rotation about the C(=O)O bond to the higher energy anti-conformer (**16′**) before cyclization can occur.

Structural studies of phenyl benzoate further tell us that it not only prefers the *syn*-ester conformation but also that the plane of the O−Ph ring is twisted some 65° out of that of the rest of the molecule as in **27**.[26,27] If this twist persists in the higher energy anti-conformation, then once radical **16** is in the anti-conformation (**16′**), it will be ideally set up for cyclization as in **28**. However, such a twist would mean that the radical (**23**) derived from **21** is not poised for cyclization even when in the anti-conformation (**29**). Indeed, for the cyclization of **21** to occur the derived radical **23** must adopt either conformation **30**, a high-energy conformation on the pathway for interconversion of the *syn*- and *anti*-ester minima, or an *anti*-ester conformation **31** in which the benzoate Ph ring has rotated out of the plane of the carbonyl group. Evidently, these dynamics are so unfavorable as to effectively preclude the cyclization of **21**.



We now return to the question of the catalytic effect of benzeneselenol on the propagation sequence. The effect is real, whether the additions are intra- or intermolecular, as is clearly seen from the effect on chain propagation, as reflected in substrate consumption, in each of the three examples studied. Moreover, the much higher yields of cyclohexadienes isolated in the presence of benzeneselenol strongly suggest that the effect does arise from quenching of cyclohexadienyl radicals by the selenol. The C−H bond dissociation energy for 1,4-cyclohexadiene is 73 ± 2 kcal mol^{-1} [28] and that for Sn−H in trimethyltin hydride 74 kcal mol^{-1},[29] from which it is seen that propagation by tin hydride would be essentially thermoneutral. Estimates for the Se−H bond dissociation energy in benezeneselenol have varied widely from 67 to 74 kcal mol^{-1},[13,30] but it has recently been determined, at least for the gas phase, to be 78 ± 4 kcal mol^{-1} using a mass spectrometric method.[31] Evidently, the reaction in question is at best borderline thermoneutral and likely slightly exothermic, yet it apparently proceeds and much better than chain transfer with tin hydride. Fully conscious of the controversy surrounding Robert's concept of polarity reversal catalysis,[32] we suggest that the rate of hydrogen atom transfer from the selenol is accelerated by substantial polarization at the transition state as depicted in **32** and correspondingly that abstraction of hydrogen from the stannane by the cyclohexadienyl radical is retarded by unfavorable polar effects. The whole sequence is driven in the forward direction by the combination of eq 2, which regenerates the selenol, and by the irreversible removal of the stannyl radical in the form of a stannyl halide (eq 3). Whatever the reason for the rate acceleration, it is evident that any further stabilization of the cyclohexadienyl radical will render the chain transfer step with the selenol significantly endothermic and therefore less likely. Thus, those cy-

(22) (a) Scaiano, J. C.; Stewart, L. C. *J. Am. Chem. Soc.* **1983**, *105*, 3609. (b) Levy, A.; Meyerstein, D.; Ottolenghi, M. *J. Phys. Chem.* **1973**, *77*, 3044−3047.

(23) 86% total addition products; only 2% of material unaccounted for which may be cyclization derived materials.

(24) Migita, T.; Takayama, K.; Abe, Y.; Kosugi, M. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1137−1142.

(25) (a) Bourn, A. J. R.; Gillies, D. G.; Randall, E. W. *Tetrahedron* **1966**, *22*, 1825−1829. (b) Nagarajan, K.; Nair, M. D.; Pillai, P. M. *Tetrahedron* **1967**, *23*, 1683−1690. (c) Azumaya, I.; Kagechika, H.; Yamaguchi, K.; Shudo, K. *Tetrahedron* **1995**, *51*, 5277−5290.

(26) Adams, J. M.; Morsi, S. E. *Acta Crystallogr. Sect B* **1976**, B32, 1345−1347.

(27) Le Fevre, R. J. W.; Sundaram, A. *J. Chem. Soc.* **1962**, 3904−3915.

(28) Burkey, J. J.; Majewski, M.; Griller, D. *J. Am. Chem. Soc.* **1986**, *108*, 2218−2221.

(29) Griller, D.; Kanabus-Kaminska, J. M.; Maccoll, A. *J. Mol. Struct. (THEOCHEM)* **1988**, *163*, 125−131.

(30) Newcomb, M.; Manek, M. B.; Glenn, A. G. *J. Am. Chem. Soc.* **1991**, *113*, 949−958.

(31) Leeck, D. T.; Li, D. T.; Chyall, L. J.; Kenttamaa, H. I. *J. Phys. Chem.* **1996**, *100*, 6608−6611.

(32) (a) Allen, R. P.; Roberts, B. P.; Willis, C. R. *J. Chem. Soc., Chem. Commun.* **1989**, 1387−1388. (b) Roberts, B. P. *J. Chem. Soc.*, Perkin Trans. 2 **1996**, 2719−2725. (c) Roberts, B. P.; Steel, A. J. *J. Chem. Soc.*, Perkin Trans. 2 **1994**, 2155−2162. (d) Zavitsas, A. A.; Chatgilialoglu, C. *J. Am. Chem. Soc.* **1995**, *117*, 10645−10654. (e) Zavitsas, A. A. *J. Chem. Soc., Perkin Trans. 2* **1996**, 391−393.

clohexadienyl radicals arising from the formal 6-endo pathway (**6** and **20**), which benefit from extra stabilization by the heteroatom, are apparently not quenched by the selenol but eventually undergo oxidation with the formation of the aromatized products **9** and **14**, respectively.

Finally, we draw attention to the fact that the inclusion of catalytic benzeneselenol in these reaction mixtures does not significantly increase the proportion of the direct reduction products (**4**, **11**, and **22**). This is in line with our previous observations when we noted that the stannane-mediated trapping of neither aryl nor vinyl radicals is accelerated by the presence of catalytic selenol.[13] This may be indicative of unfavorable polar effects at the transition state for hydrogen abstraction from selenols by σ-type radicals.[13] Alternatively, it may simply reflect the fact that the rate constant for the quenching of aryl radicals by tributyltin hydride already approaches the diffusion controlled limit[33] and so leaves little room for further acceleration.[13]

Experimental Section[34]

Reaction of *o*-Iodo-*N*-methylbenzanilide (1) with Bu_3SnH. To a solution of *o*-iodo-*N*-methylbenzanilide[8] **1** (0.5 g, 1.48 mmol) in benzene (150 mL) at reflux under Ar was added a solution of Bu_3SnH (0.48 mL, 1.8 mmol) and AIBN (32 mg, 0.22 mmol) in benzene (60 mL) dropwise by means of a syringe pump over 20 h. After a further 1 h at reflux, the reaction mixture was cooled to room temperature and the solvent removed under reduced pressure. The crude reaction mixture, taken up in acetonitrile, was washed with petroleum ether, evaporated, and purified by chromatography on silica gel (eluent hexanes:ether 3:1) to give **4** (71 mg, 23%), **9** (37 mg, 12%), and recovered **1** (184 mg, 37%). *N*-Methylbenzanilide **4**: mp 183−186 °C (lit.[35] mp 185−187 °C); ^{1}H NMR δ 3.49 (3H, d, J = 1.3 Hz), 7.02 (2H, app d, J = 7.0 Hz), 7.09−7.23 (6H, m), and 7.28 (2H, m); ^{13}C NMR δ 38.3, 126.4, 126.8 (2C), 127.6 (2C), 128.6 (2C), 129.0 (2C), 129.5, 135.8, 144.8, and 170.6. *N*-Methyl-6(5*H*)-phenanthridinone **9**: mp 104−106 °C (lit.[8] mp 108.5 °C): ^{1}H NMR δ 3.79 (3H, s), 7.30 (1H, t, J = 8.0 Hz), 7.38 (1H, d, J = 8.2 Hz), 7.55 (2H, m), 7.74 (1H, dt, J = 1.3 and 8.3 Hz), 8.24 (2H, d, J = 8.67 Hz), and 8.53 (1H, d, J = 7.9 Hz); ^{13}C NMR δ 20.9, 115.0, 119.1, 121.5, 122.4, 125.5, 127.8, 128.8, 129.5, 132.3, 133.4, 137.9, and 161.5.

Reaction of *o*-Iodo-*N*-methylbenzanilide (1) with Bu_3SnH and PhSeSePh. The above experiment was repeated with the difference being that PhSeSePh (92 mg, 0.30 mmol) was added to the initial solution of **1** in benzene before addition of Bu_3SnH commenced. Isolation and chromatographic purification as above provided **4** (74 mg, 22%), **9** (68 mg, 22%), and **7** (134 mg, 43%). Spirolactam **7**, an oil, had spectral characteristics in full agreement with the literature:[36] ^{1}H NMR δ 2.90 (5H, m), 5.27 (2H, dt, J = 10.3 and 2 Hz), 6.26 (2H, dt, J = 10.2 and 3.3 Hz), 7.25 (1H, dd, J = 6.9 and 0.8 Hz), 7.4−7.53 (2H, m), and 7.8 (1H, dd, J = 6.8 and 0.6 Hz); ^{13}C NMR δ 25.0, 25.9, 63.2, 123.0, 123.1, 125.6 (2C), 128.3, 129.5 (2C), 131.2, 131.5, 149.7, and 167.5.

Reaction of Phenyl 2-Iodobenzoate (10) with Bu_3SnH. To a solution of phenyl 2-iodobenzoate **10**[37] (0.42 g, 1.3 mmol) in benzene (65 mL) at reflux under Ar was added a solution of Bu_3SnH (0.45 mL, 1.69 mmol) and AIBN (22 mg, 0.13 mmol) in benzene (20 mL) dropwise by means of a syringe pump over 15 h. After a further 1 h at reflux, the reaction mixture was cooled to room temperature and the solvent removed under reduced pressure. The crude reaction mixture was taken up in acetonitrile and washed with petroleum ether and then evaporated under reduced pressure and purified by chromatography on silica gel (eluent hexanes:ether 10:1) to give the reduced product **11** (64 mg, 25%), the 6-endo product **14** (13 mg, 5%), and biphenyl **15** (6 mg, 3%), together with recovered starting material (**10**) (113 mg, 27%). Phenyl benzoate (**11**): mp 66−67 °C (lit.[38] mp 66−68 °C); ^{1}H NMR δ 7.20−7.32 (3H, m), 7.42 (2H, app t, J = 7.4 Hz), 7.53 (2H, app t, J = 7.5 Hz), 7.65 (1H, 2H, tt, J = 1.3 and 7.4 Hz), and 8.24 (2H, dt, J = 7.1 and 1.7 Hz); ^{13}C NMR δ 121.9 (2C), 125.8, 128.5 (2C), 129.4, 130.1 (2C), 133.5, 150.9, and 165.1. Benzo[*c*]chromen-6-one (**14**): mp 91−92 °C (lit.[38] mp 89−92.5 °C); ^{1}H NMR δ 7.35 (2H, m), 7.50 (1H, dt, J = 1.4 and 7.1 Hz), 7.60 (1H, t, J = 8.0 Hz), 7.81 (1H, dt, J = 1.3 and 7.7 Hz), 8.04 (1H, dd, J = 1.4 and 8.1 Hz), 8.10 (1H, d, J = 8.0 Hz), and 8.38 (1H, d, J = 7.8 Hz); ^{13}C NMR δ 117.7, 117.9, 121.1, 121.6, 122.7, 124.5, 128.8, 130.4, 130.5, 134.7, 134.8, 151.2, and 161.2. Biphenyl (15): mp 69−70 °C; ^{1}H NMR δ 7.35 (2H, tt, J = 7.3 and 1.4 Hz), 7.46 (4H, t, J = 7.1 Hz), and 7.60 (4H, d, J = 7.3 Hz); ^{13}C NMR δ 127.1 (2C), 127.2, 128.7 (2C), and 141.2.

Reaction of Phenyl 2-Iodobenzoate (10) with Bu_3SnH and PhSeSePh. The above experiment was repeated with the difference being that PhSeSePh (80 mg, 0.26 mmol) was added to the initial solution of **10** in benzene before addition of Bu_3SnH commenced. Isolation and chromatographic purification as above provided an inseparable mixture of **12** and **13** (143 mg, 40%, 6.8:1), **11** (44 mg, 17%), **14** (31 mg, 12%), and biphenyl **15** (42 mg, 21%). Phenyl 2-(cyclohexadienyl)benzoate (**12** and **13**): ^{1}H NMR, major isomer (**12**) δ 2.78 (2H, m), 5.03 (1H, m), 5.85 (4H, m), 7.2−7.42 (4H, m), 7.42−7.6 (4H, m), and 8.12 (1H, dd, J = 7.4 and 1.4 Hz); minor isomer (**13**) δ 2.38 (1H, m), 2.78 (1H, m), 4.63 (1H, m), and 5.68−6.15 (4H, m), 8.25 (1H, d, J = 7.5 Hz); ^{13}C NMR, major isomer (**12**) δ 25.7, 37.9, 121.7 (2C), 124.0 (2C), 125.9, 126.2, 128.3 (2C), 128.5, 129.5 (2C), 130.4, 130.6, 132.8, 146.9, 150.8, and 166.1; minor isomer (**13**) δ 31.3, and 35.9; HRMS calcd for $C_{13}H_{11}O$ ($M^{+\bullet}$ − PhO$^\bullet$) 183.0810, found 183.0756.

Reaction of 2-Iodophenyl Benzoate (21) with Bu_3SnH. To a solution of 2-iodophenyl benzoate **21**[39] (0.43 g, 1.3 mmol) in benzene (65 mL) at reflux under Ar was added a solution of Bu_3SnH (0.45 mL, 1.69 mmol) and AIBN (22 mg, 0.13 mmol) in benzene (20 mL) dropwise by means of a syringe pump over 15 h. After a further 1 h at reflux, the reaction mixture was cooled to room temperature and the solvent removed under reduced pressure. The crude reaction mixture, taken up in acetonitrile, was washed with petroleum ether and then evaporated under reduced pressure and purified by chromatography on silica gel (eluent hexanes:ether 10:1) to give the reduced product **22** (21 mg, 8%), **26** (131 mg, 37%), and recovered starting **21** (138 mg, 32%). *o*-Biphenyl benzoate (**26**): mp 76−77 °C (lit.[40] 73−76 °C); ^{1}H NMR δ 7.27−7.50 (11H, m), 7.59 (1H, tt, J = 0.6 and 7.4 Hz), and 8.05 (2H, td, J = 0.7 and 7.24 Hz); ^{13}C NMR δ 123.0, 126.3, 127.3, 128.2 (2C), 128.38 (2C), 128.44, 128.9 (2C), 129.3, 130.0 (2C), 130.9, 133.3, 134.9, 137.4, 147.7, and 165.0.

Reaction of 2-Iodophenyl Benzoate (21) with Bu_3SnH and PhSeSePh. The above experiment was repeated with the difference that PhSeSePh (80 mg, 0.26 mmol) was added to the initial solution of **21** in benzene before addition of Bu_3SnH commenced. Isolation and chromatographic purification as above provided an inseparable mixture of **24** and **25** (276 mg, 77%), **22** (31 mg, 12%), and **26** (28 mg, 8%). **24** and **25**: ^{1}H NMR, major isomer (**24**) δ 2.7 (2H, m), 4.25 (1H, m), 5.70−5.87 (4H, m), 7.2−7.45 (4H, m), 7.54 (2H, t, J = 6.6 Hz), 7.66 (1H, t, J = 7.5 Hz), and 8.24 (2H, dd, J = 0.9 and 7.0 Hz); minor isomer (25) δ 2.35−2.42 (1H, m), 2.50−2.62 (1H, m), 3.89 (1H, m), 5.70−6.10 (4H, m), and 7.44 (2H, t, J = 8.1 Hz); ^{13}C NMR, major isomer (**24**): δ 25.6, 35.7, 122.4, 124.3 (3C), 126.5, 127.2 (2C), 127.4, 128.6 (2C), 130.0,130.1(2C), 133.6, 134.8, 148.3, and 165.2; minor isomer (**25**) δ 30.1, 33.6,121.7 (2C), 122.6, 123.7, 124.8,

(33) At ambient temperatures the rate constant for hydrogen abstraction from Bu_3SnH by a phenyl radical is 7.8×10^8 M^{-1} s^{-1}. At 80 °C it is estimated to be $\sim 1.0 \times 10^9$ M^{-1} s^{-1}: Garden, S. J.; Avila, D. V.; Beckwith, A. L. J.; Bowry, V. W.; Ingold, K. U.; Lusztyk, J. *J. Org. Chem.* **1996**, *61*, 805−809.

(34) For the general experimental part, see footnote 13a.

(35) von Braun, J.; Weisbach, K. *Chem. Ber.* **1930**, *63*, 489−497.

(36) Hey, D. H.; Jones, G. H.; Perkins, M. J. *J. Chem. Soc. (C)* **1971**, 116−122.

(37) Singh, A.; Andrews, L. J.; Keefer, R. M. *J. Am. Chem. Soc.* **1962**, *84*, 1179−1185.

(38) Heacock, R. A.; Hey, D. H. *J. Chem. Soc.* **1954**, 2481−2484.

(39) Buchan, S.; McCombie, H. *J. Chem. Soc.* **1931**, 137−144.

(40) Wenkert, E.; Barnett, B. F. *J. Am. Chem. Soc.* **1960**, *82*, 4671−4675.

125.4, 125.9, 126.2, 128.9, 129.2, 129.3, 129.5 (2C), 133.5, 137.4, 149.7, and 164.5; HRMS calcd for $C_{19}H_{16}O_2$ 276.1150, found 276.1133.

Acknowledgment. We thank the NSF (CHE 9625256) for support of this work and Dr. Qingwei Yao for a preliminary experiment.

Supporting Information Available: copies of ^1H and ^{13}C NMR spectra for the mixture of **12** and **13** and of **24** and **25** (4 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.

JO972197S