$PhSeSiR_3$-Catalyzed Group Transfer Radical Reactions

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A novel design for initiating radical-based chemistry in a catalytic fashion is described. The design of the concept is based on the phenylselenyl group transfer reaction from alkyl phenyl selenides by utilizing $PhSeSiR_3$ (**1**) as a catalytic reagent. The reaction is initiated by the homolytic cleavage of −C−Se− bond of an alkyl phenyl selenide by the in situ generated alkylsilyl radical ($R_3Si^{\bullet}$), obtained by the mesolysis of $PhSeSiR_3]^{\bullet-}$ (**1**$^{\bullet-}$). The oxidative dimerization of counteranion $PhSe^-$ to PhSeSePh functions as radical terminator. The generation of **1**$^{\bullet-}$ is achieved by the photoinduced electron transfer (PET) promoted reductive activation of **1** through a photosystem comprising of a visible-light (410 nm)-absorbing electron rich DMA as an electron donor and ascorbic acid as a co-oxidant (Figure 1). The optimum mole ratio between the catalyst **1** and alkyl phenyl selenides for successful reaction is established to be 1:10. The generality of the concept is demonstrated by carrying out variety of radical reactions such as cyclization (**10, 15**−**18**), intermolecular addition (**25**), and tandem annulations (**32**).

Introduction

The use of tin-based reagents in free radical chemistry has dominated the scene ever since the original discovery of the radical generation by organotin hydrides (X_3SnH);[1] this dominance has been rightly referred to, recently, as "Tyranny of Tin",[2] despite their drawbacks such as cost, instability, toxicity,[3] loss of valuable functionality due to the termination of radical sequence by irreversible H-abstraction,[4] and the difficulty encountered in removing the tin byproducts from the residue[5] whose disposal poses hazardous problem. Although partial solution to some of these problems have been addressed by introducing many new reagents,[2,6] atom/group transfer reactions,[7,8] and several other approaches,[9] the initiation step in all these approaches invariably requires stoichiometric use of the reagents. Since there is growing demand to reduce the amount of toxic wastes and byproducts arising out of chemical reactions,[10] increasing emphasis is laid on the invention and development of a catalytic and environmentally compatible strategy for initiating radical-based chemistry owing to its ever increasing popularity among synthetic chemists. Significant progress has also been made, recently, toward developing newer methodologies for initiating radical-based reactions in catalytic manner, utilizing either tin hydride reagents catalytically[11] or its in situ generation[12] or use of titanocene-catalyzed reductive ring opening of an epoxide;[13] however, considering the importance of radical reactions in organic synthesis, introduction of another catalytic strategy could be a welcome addition in the repertoire of organic chemists.

We have reported[14] an efficient strategy for the generation of phenyl selenide anion ($PhSe^-$) and alkylsilyl radical ($R_3Si^{\bullet}$) by the mesolysis[15] of $PhSeSiR_3^{\bullet-}$, produced by the visible-light (410 nm)-initiated photoinduced electron transfer (PET) activation of $PhSeSiR_3$ (R = *tert*-butyldiphenyl) through the photosystem as shown in Figure 1. The significantly higher rate constant (9.6×10^7 M^{-1} s^{-1})[6b] for the reaction of $R_3Si^{\bullet}$ with alkyl phenylselenides and fast oxidative dimerization of $PhSe^-$ to PhSeSePh, an excellent radical scavenger[16] (the rate

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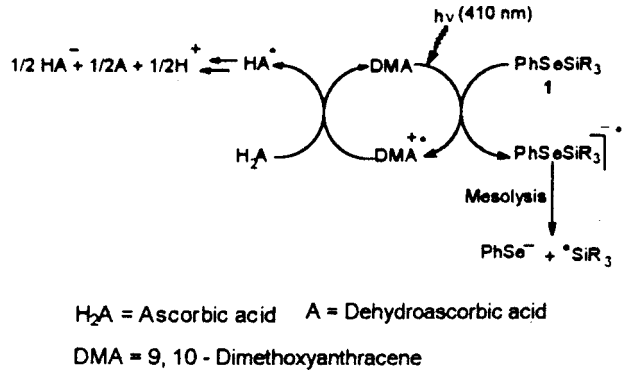


Figure 1. PET reductive activation of $PhSeSiR_3$.

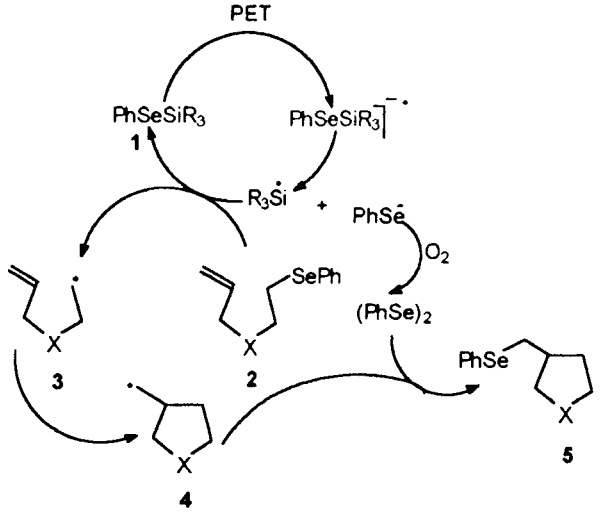


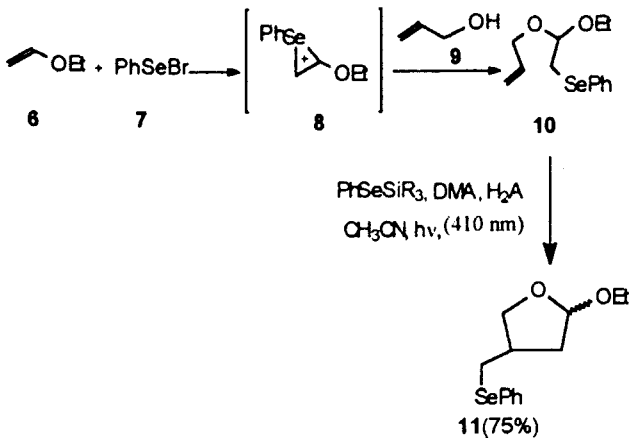
Figure 2. A catalytic strategy for the group transfer radical reactions.

constant for the S_H2 attack of 5-hexenyl radical upon PhSeSePh is calculated to be 1.2×10^7 M^{-1} s^{-1}),[17] led us to envision that a catalytic strategy for phenylselenyl group transfer radical-based reactions might be possible to effect from a precursor of type **2** through a cycle as shown in Figure 2**.** Additional advantage of this strategy was perceived by the stability of the precursors as well as products and the various avenues available for the transformation of the products. The success of our effort is delineated in this article.

Results and Discussion

Design, Optimization and Generalization of the Concept. To introduce a concept of catalytic group transfer radical reaction in organic synthesis, a design as depicted in Figure 2 was visualized. Initially, we decided to investigate the phenylselenyl group transfer radical cyclization reaction of **10**, prepared in 80% yield by the reaction of PhSeBr (**7**) with ethyl vinyl ether (**6**) in the presence of allyl alcohol (**9**).[18] To ensure that the PET activation of a mixture containing **1** and **10**, utilizing the photosystem as shown in Figure 1, selectively generates $\mathbf{1}^{\bullet-}$, ΔG_{et} values for the formation of $\mathbf{1}^{\bullet-}$ (−181 kJ M^{-1})[14] as well as $\mathbf{10}^{\bullet-}$ (−80 kJ M^{-1}) were compared. The ΔG_{et} value for the formation of $\mathbf{10}^{\bullet-}$ was estimated

Scheme 1. Preparation of 10 and Its PET Activation



through Weller equation[19] employing the values of $E_{1/2}^{ox}$ (DMA) as 0.98 eV,[20] $E_{1/2}^{red}$ of **10** as −1.4 eV, estimated by cyclic voltammetry utilizing an identical experimental setup as described elsewhere[14] and $E_{0,0}$ of DMA as 3.21 eV.[21] Since the selectivity of the radical ion generation from a mixture of potential electron donors/acceptors depend on the magnitude of ΔG_{et} values associated with the electron-transfer processes,[22,23] the large difference between the ΔG_{et} values for the formation of $\mathbf{1}^{\bullet-}$ vs $\mathbf{10}^{\bullet-}$ indicated that there will be selectivity in the formation of $\mathbf{1}^{\bullet-}$ if a mixture of **1** and **10** were activated. This study coupled with the known[14] mesolytic characteristics of $\mathbf{1}^{\bullet-}$ (producing $R_3Si^{\bullet}$ and $PhSe^-$) and significantly higher quantum yield of disappearance of **1** ($\phi_{dis} = 0.223$)[24] in comparison to ϕ_{dis} for −C−Se− bonds (≈0.054)[25] convinced us that PET activation of a mixture of **1** and **10** through the photosystem as shown in Figure 1 would initiate a radical reaction from **10** by chalcogen transfer to $R_3Si^{\bullet}$ while regenerating **1** in the process as shown in Figure 2. The reorganization of the radical followed by its termination by PhSeSePh, produced by the oxidative dimerization of $PhSe^-$, would set off a catalytic cycle for the formation of **11** through the steps as shown in Figure 2. With this premise, we began our study first by establishing the catalytic role of **1** in the above reaction.Toward this endeavor, PET activation of **10** at different concentrations (0.18, 0.27, and 0.35 mmol) with a fixed concentration of **1** (0.018 mmol), DMA (0.11 mmol), and H_2A (0.32 mmol) was studied by irradiating 50 mL solution of each in Pyrex test tubes at 410 nm (450-W Hanovia lamp, NH_3−$CuSO_4$ solution).[26] Progress of the reaction was monitored by HPLC analysis. After 45 min of irradiation (consumption of **10**, ≈55−60%), the solutions in the test tubes were analyzed by HPLC which showed negligible change in the concentration of **1** as well as DMA in the tube having **10** and **1** in 10:1 mole ratio. This study was not performed at higher consumption of

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(26) Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1973; p 124.

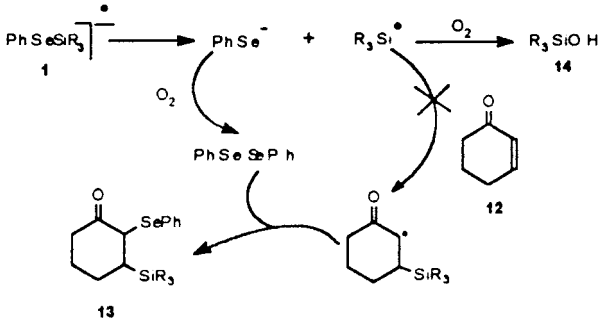
10 to avoid competitive reaction by the product **11**. In other test tubes, the consumption of **10** was not found linearly related with the concentration of **1,** probably due to the interference of **10** with the light absorbance of DMA. Therefore, based on the above study, it may be suggested that the present catalytic group transfer radical reaction strategy can be best performed at 10:1 mole ratio of the substrate (**10**) to catalyst (**1**).

Preparative PET reaction by irradiating (410 nm, 450-W Hanovia lamp, $CuSO_4$:NH_3 filter)[26] a mixture containing **10** (0.76 mmol), DMA (0.30 mmol), ascorbic acid (0.88 mmol), and **1** (0.08 mmol), followed by usual workup and column chromatographic purification of the residue, gave **11** in 75% yield (Scheme 1**)**. Although, quantitative estimation of recovered DMA and **1** was not made after column chromatography, negligible change in their concentrations, after the photolysis was completed, was established by comparing the HPLC analysis of the photolyzate before and after the irradiation. The accumulated concentration of PhSeSePh in the reaction mixture at a given time, also determined by HPLC analysis of the aliquots withdrawn at different intervals of time during photolysis, was found to be very small, indicating that the combined rates of generation and cyclization[27] of 3-oxa-5-hexenyl radical of type **3** from **10** is possibly slower than the rate of oxidative dimerization of $PhSe^-$ to PhSeSePh.[28]

To provide some conclusive support to the mechanism for the catalytic cycle as proposed in Figure 2, the possibilities of other competing reaction pathways available to the radical intermediates must be eliminated. For example, the alkyl radical **4** could possibly terminate by chalcogen transfer either from PhSeSePh or from **2.** However, based on the comparative rate constant values of chalcogen transfer from PhSeSePh ($k = 2.6 \times 10^7$ $M^{-1}s^{-1}$) and alkyl selenide ($k = 1.0 \times 10^5$ M^{-1} s^{-1}) to an octyl radical, reported by Curran et al.[29] and their conclusion that diselenide would usually be the preferred reagent for the termination of an alkyl radical in such cases, the involvement of the later possibility can easily be ignored. Furthermore, if **4** is presumed to be terminating by chalcogen transfer from **2,** a radical chain reaction would have set in for the transformation of **10** → **11**. However, our observation that the conversion of **10** → **11** is very much dependent on the irradiation time supports the termination of **4** by chalcogen transfer by PhSeSePh and not by alkyl-SePh. The PhSe$^\bullet$, generated after the termination of cyclized alkyl radical derived from **10** by PhSeSePh, dimerizes efficiently ($k_r = 7.0 \times 10^9$ M^{-1} s^{-1})[30] to PhSeSePh as the slower rate of reaction of PhSe$^\bullet$ with an olefinic bond and its known[30] reversibility rules out any other competing decay mode.

The possible decay of alkyl radical **4** as well as *tert*-butyldiphenylsilyl radical ($R_3Si^\bullet$) by the reaction of molecular oxygen could also be ruled out on the following considerations. The reaction of an alkyl radical with

Scheme 2. Selenosilylation Reaction of Cyclohexenone



molecular oxygen is diffusion-controlled ($k = 4.9 \pm 0.6 \times 10^9$ M^{-1} s^{-1} for cyclopentyl radical),[31] and the rate-determining step is the termination of the resultant peroxy radical (ROO$^\bullet$) by hydrogen abstraction[32] and not the reaction of alkyl radical with oxygen. Therefore, the reaction of **4** with oxygen, if it occurs at all, could be reversible,[33] as there is no possibility of H-abstraction by the corresponding peroxy radical. Moreover**,** we were unable to detect any product related to the peroxy radical derived from **10**. Since, no kinetic data, to the best of our knowledge, is available on the reaction of $R_3Si^\bullet$ with O_2 in the solution phase (the rate constant for the reaction of $Me_3Si^\bullet$ with O_2 is reported[34] to be $\approx 1.0 \times 10^{10}$ M^{-1} s^{-1} in gas phase), no definite statement could be made about the rate constants for the reaction of *tert*-butyldiphenylsilyl radical with oxygen in comparison to the oxidative dimerization rate constant of $PhSe^-$ to PhSeSePh.[28] However, in a separate study,[35] where we were attempting to study the selenosilylation of an enone **12** through the route as shown in Scheme 2, *tert*-butyldiphenylsilanol (R_3SiOH, **14**) was obtained as the major product. The absence of **14** during the transformation of **10** → **11** suggests that the rate of chalcogenide transfer from alkyl-SePh to $R_3Si^\bullet$ could be much higher than the reaction rate of $R_3Si^\bullet$ with molecular oxygen.

To compare the efficiency of this methodology over the one earlier reported by us[25] by the direct PET activation of −C−Se− bond compounds, a control experiment was performed in a similar manner as described above but without having **1** in the reaction mixture. The comparative results indicated that, within the constant period of irradiation, the efficiency for the formation of **11** in the tube containing **1** was at least 4−5 times higher than the one without **1**. This observation was expected due to the higher quantum efficiency of −Se−Si− bond dissociation from its corresponding radical anion (**1**$^{\bullet-}$, $\phi_{dis} = 0.223$)[24] in comparison to ϕ_{dis} of −C−Se− bonds (≈ 0.054)[25] and high rate constant of −C−Se− bond dissociation by $R_3Si^\bullet$ (9.6×10^7 M^{-1} s^{-1}).[6b]

To establish the generality of the catalytic phenylselenyl group transfer radical cyclization reactions, a number of substrates (**15**−**18)** were studied, and the results are given in Table 1. The starting substrates (**15**−

(27) The rate constant for the cyclization of 3-oxa-5-hexenyl radical is reported to be 9.0×10^6 M^{-1} s^{-1}; Newcomb, M.; Filipkowski, M. A.; Johnson, C. C. *Tetrahedron Lett*. **1995**, *36*, 3643.

(28) Although, the rate constant for the oxidative dimerisation of $PhSe^-$ to PhSeSePh is not known, it is understood to be much higher than the oxidative dimerization of PhSeH. *Encyclopaedia of Reagents in Organic Synthesis*; Paquette, L. A., Ed.; John Wiley & Sons: New York, 1995; Vol. 1, p 270.

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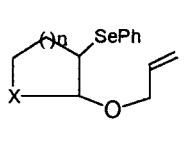
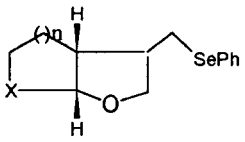
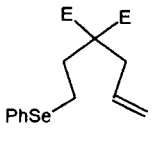
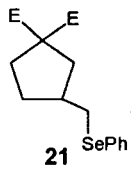
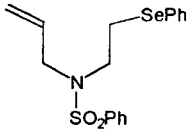
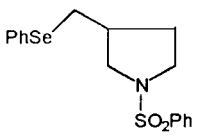
(34) Niiranen, J. T.; Gutman, D. *J. Phys. Chem*. **1993**, *97*, 4106.

(35) Pandey, G.; Rao, K. V. N. Unpublished result.

Table 1. Phenylselenyl Group Transfer Radical Reaction

Entry	Substrate[i]	Product[ii]	Yield(%)[iii]
1	 **15**. n = 1; X = CH_2	 **19**	77
2	**16**. n = 2; X = O	**20**	82
3	 **17**	 **21**	73
4	 **18**	 **22**	64

[i] See Supporting Information for the preparation and characterizations of **17** and **18**. [ii] Characterized by ^{1}H NMR, ^{13}C NMR, and mass spectral analyses. [iii] Isolated yield, unoptimized.

18) were obtained by following the reported procedures with little or no modification.[36]

Intermolecular additions and Tandem Annulation Reactions. The spectacular success of the catalytic phenylselenyl group transfer radical cyclization reaction of **10** through the cycle, as shown in Figure 2, encouraged us to evaluate further the scope of this strategy for other contemporary radical reactions such as intermolecular additions and tandem annulations. Intermolecular radical additions, though, are powerful tools in preparative organic chemistry, have difficulty in their execution by classical radical-based methodology due to competing bimolecular side reactions.[37] Moreover, with stannous-based reactions the difficulty lies, apart from being ecologically noncompatible, in preventing premature H-atom transfer to the radical before it adds to the olefin.[38] The other alternative approaches known in this context also lack flexibility in the choice of radical precursors.[39,40] Therefore, it occurred to us that application of our methodology, through the sequences as shown in Figure 3, could provide an attractive route in catalytic manner for the group transfer intermolecular radical addition reaction where bimolecular radical reactions

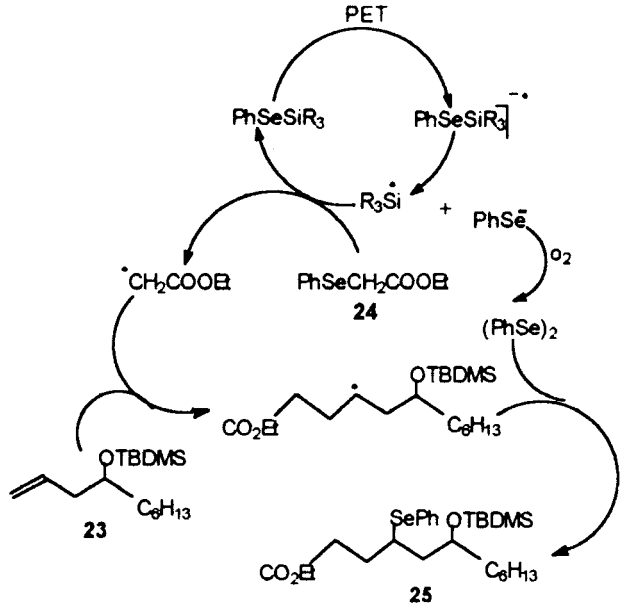
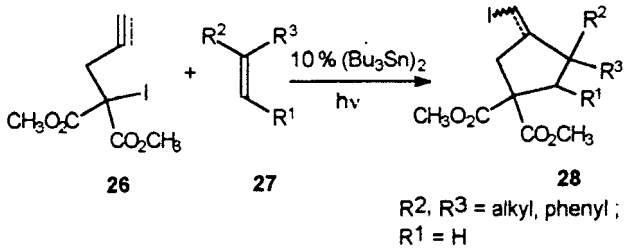


Figure 3. Catalytic intermolecular phenylselenyl group addition.

Scheme 3. Iodine Atom Transfer Strategy for the Construction of Five-Membered Rings.



would be diminished due to fast termination of the adduct radical by phenylselenyl group transfer ($k = 3 \times 10^7$ M^{-1} s^{-1} for secondary alkyl radicals).[41] Toward this endeavor, we studied the addition of $PhSeCH_2COOEt$ (**24**) onto the 4-*tert*-butyldimethylsilyloxy-1-decene (**23**). Considering the favorable electron pairing (electron-poor radical/electron-rich acceptor) PET reaction of a mixture containing **1** (0.18 mmol), **24** (1.85 mmol), **23** (1.85 mmol), DMA (0.63 mmol), and ascorbic acid (1.57 mmol) followed by workup and purification gave **25** as a yellow oil in 61% yield (Figure 3). Product **25** was characterized by ^{1}H NMR, ^{13}C NMR, and mass spectral data.

The *exo*-mode cyclization property of 5-hexenyl radicals have been widely utilized for the construction of five-membered carbocyclic rings.[37] Curran et al. have also reported[42] in situ generation and iodine atom transfer cyclization of 5-hexenyl radicals via addition/cyclization sequence (annulation) from **26** to a variety of simple olefins (**28**) to construct five-membered ring systems (Scheme 3). However, construction of six-membered carbocyclic ring systems, also widely distributed in numerous biologically active molecules, by *endo*-mode radical cyclizations has been known to be difficult.[37]

The presence of silicon atom α as well as β to a carbon-centered radical is known[43] to reverse the regioselectivity of radical cyclizations (favoring the *endo*-mode) due to

(36) (a) For the preparation of compound **15** and **16**, see: Engman, L.; Gupta, V. *J. Org. Chem.* **1997**, *62*, 157 whereas compound **17** was prepared by the nucleophilic displacement of phenylselenyl anion on the corresponding bromide (cf: Sharpless, K. B. *J. Am. Chem. Soc.* **1973**, *95*, 2697). (b) For the preparation of compound **18**, see: Padwa, A.; Nimmesgern, H.; Wong, G. S. K. *J. Org. Chem.* **1985**, *50*, 5620.

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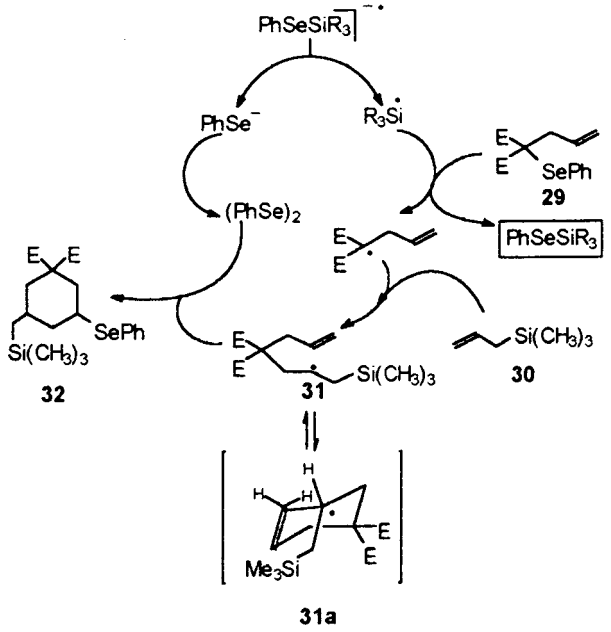

Figure 4. Strategy for *endo-trig* cyclization in radical reactions.

the involvement of seemingly less dipolar transition state structure compared to normal carbon-centered radical cyclizations. Though this study has been shown only with an example where cyclization places a silicon atom in the ring, it occurred to us that if these observations are general, a tandem addition/cyclization reaction between **29** and allyltrimethylsilane (**30**) should provide six-membered carbocyclic ring system **32** by *endo*-cyclization of the intermediate **31** via expected transition state structure **31a**. The success of this concept was also expected to provide an option to organic chemists for manipulation of the regiochemistry of radical reactions during carbocyclization reactions. With this background, we studied the PET activation of a mixture containing **1** (0.15 mmol), **29** (1.4 mmol), DMA (0.63 mmol), ascorbic acid (1.62 mmol), and allyltrimethylsilane (**30**) (3.5 mmol) which gave, to our pleasant surprise, only compound **32** in good yield (65%) (Figure 4). All the spectral characterizations of **32** indicated it to be a pure diastereomer; however, we did not try to ascertain its exact stereochemistry.

In conclusion, a conceptually new and ecologically compatible[44] approach for initiating a catalytic phenylselenyl group transfer radical reaction, in general, has been designed and developed. The development of this strategy is expected to add new dimensions to radical-based chemistry.

Experimental Section

General. DMA[45] and PhSeSiR$_3$[46] were synthesized and purified by following the literature procedures.

Irradiations were performed in a specially designed double-walled photoreactor. The photoreactor consisted of three chambers. The first and outermost chamber contained irradiation solution while the second one was charged with $CuSO_4 \cdot 5H_2O$:NH_3 filter solution. This filter solution allowed only 410 nm wavelength light to pass through.[26] A 450-W Hanovia medium-pressure mercury vapor lamp was used as light source that was housed in a water-circulated double-jacketed chamber immersed into the second chamber, maintaining a 1 cm path length of the filter solution. The whole photoreactor was made of Pyrex glass.

Evaluation of Catalytic Property of 1. A 200 mL stock solution in acetonitrile containing **1** (0.07 mmol), DMA (0.42 mmol), and ascorbic acid (0.31 mmol) was prepared. Fifty milliliter amounts of this solution were distributed into three test tubes made up of Pyrex glass, and 0.05 g (0.176 mmol), 0.075 g (0.265 mmol), and 0.1 g (0.35 mmol) of **10** were introduced into each test tube resulting in mole ratios of **10** with respect to **1** as 10:1, 15:1, and 20:1, respectively. One milliliter each of this solution was analyzed before irradiation by HPLC after adding 0.5 mL of solution of Ph_3As (0.05 M) as an internal standard, and the area ratios of **10**:Ph_3As and **1**:Ph_3As were recorded. These tubes were irradiated externally at 410 nm wavelength light coming out of a 450-W Hanovia lamp after passing through a $CuSO_4$:NH_3 filter solution. Aliquots were analyzed time to time by HPLC in the similar manner as described above, and the area ratios were compared. After 45 min, the irradiation was discontinued. The HPLC analysis of the test tube containing **10** and **1** in 10:1 mole ratio (first tube) indicated negligible change in the concentration of **1**. Formation of **11** as the only product was noticed by HPLC analysis. The other two tubes showed no correlation between the conversion of **10** and the concentration of **1**.

Preparative PET Cyclization of 10. A dilute solution of CH_3CN (500 mL) containing a mixture of **1** (0.07 g, 0.17 mmol), **10** (0.5 g, 1.74 mmol), DMA (0.15 g, 0.63 mmol), and ascorbic acid (0.28 g, 1.62 mmol) was irradiated in the special photoreactor (as described in the general Experimental Section) with a 450-W Hanovia medium-pressure mercury lamp at room temperature without removing dissolved oxygen from the solution. The progress of the reaction was monitored by HPLC. When substantial consumption of **10** was noticed, the irradiation was discontinued. Solvent was removed under vacuum and the crude photolyzate was purified by silica gel column chromatography to give a yellow oily product **11** (0.37 g, 75% yield).

11: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.15−1.30 (m, 3H), 1.60−1.80 (m, 1H), 2.15−2.60 (m, 2H), 2.90−3.17 (m, 2H), 3.30−3.50 (m, 1H), 3.57−3.80 (m, 2H), 3.95−4.10 (m, 1H), 5.10−5.17 (m, 1H), 7.20−7.30 (m, 3H), 7.45−7.55 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 132.8, 131.5, 129.9, 128.9, 127.6, 126.9, 104.0, 103.8, 72.0, 63.0, 62.8, 39.9, 39.6, 38.6, 37.9, 32.3, 31.5, 15.4, 15.3; MS *m/e* (relative intensity) 286 (M^+, 28), 240 (15), 157 (23), 91 (42), 83 (100).

Identical irradiation procedures were adopted for the PET activation of **15**−**18**, **23,** and **29,** and the spectral characterization of products **19**−**22, 25** and **32** are given as follows:

19: yield: 77%; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.45−1.90 (m, 6H), 2.00−2.20 (m, 1H), 2.55−2.75 (m, 1H), 2.85−3.15 (m, 2H), 3.30−3.50 (m, 1H), 3.95 (dd, J = 7.8, 13.5 Hz, 1H), 4.45−4.60 (m, 1H), 7.20−7.30 (m, 3H), 7.45−7.55 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 132.9, 132.6, 130.3, 130.1, 129.0, 126.9, 126.8, 86.2, 85.1, 73.3, 72.2, 50.1, 48.1, 47.1, 43.4, 34.4, 34.0, 33.0, 30.5, 26.4, 25.9, 25.2, 24.0; MS *m/e* (relative intensity) 282 (M^+, 10), 157 (15), 124 (17), 95 (78), 67(100).

20: yield: 82%; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.35−1.85 (m, 4H), 2.00−2.15 (m, 1H), 2.50−2.75 (m, 1H), 2.80−3.05 (m, 2H), 3.65−3.85 (m, 3H), 4.05 (t, J = 7.1 Hz, 1H), 5.25 (d, J =

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(44) This strategy could be considered ecologically compatible as in this approach the only molecule which undergoes chemical destruction is the ascorbic acid. No selenium-containing compound is produced as byproduct. Moreover, organoselenium compounds are known to be less toxic than their inorganic counterparts. Aromatic selenium compounds seems to be still less toxic than aliphatic selenium compounds. For detailed toxicological data on selenium compounds see: In *Selenium*; Zingaro, R. A., Cooper, C. W., Ed.; Van Nostrand Reinhold Company: New York, 1974; p 669.

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3.7 Hz, 1H), 7.20−7.35 (m, 3H), 7.45−7.60 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 133.1, 129.5, 129.0, 127.2, 101.8, 70.1, 61.0, 41.2, 37.4, 25.8, 22.9, 19.2; MS *m/e* (relative intensity) 298 (M^+, 6), 197 (20), 157 (15), 141 (50), 116 (42).

21: yield: 73%; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.25 (t, J = 7.3 Hz, 6H), 1.35−1.55 (m, 1H), 1.85−2.05 (m, 2H), 2.10−2.40 (m, 3H), 2.45−2.60 (m, 1H), 2.95 (d, J = 8.2 Hz, 2H), 4.20 (q, J = 7.3 Hz, 4H), 7.20−7.30 (m, 3H);7.45−7.55 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 172.6, 133.0, 129.3, 127.1, 61.6, 60.4, 40.9, 40.2, 34.1, 33.5, 32.6, 14.3; MS *m/e* (relative intensity) 384 (M^+, 20), 227 (52), 119 (27), 153 (100).

22: yield: 64%; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.50−1.65 (m, 1H), 1.90−2.05 (m, 1H), 2.21−2.37 (m, 1H), 2.60−2.85 (m, 2H), 2.95−3.05 (m, 1H), 3.15−3.55 (m, 3H), 7.20−7.30 (m, 3H), 7.35−7.65 (m, 5H), 7.70−7.85 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 133.0, 132.5, 129.0, 128.9, 129.4, 127.2, 53.2, 47.3, 39.1, 31.6, 30.6, 29.6; MS *m/e* (relative intensity) 381 (M^+, 4), 223 (100), 209 (13), 141 (25); HRMS calculated for $C_{17}H_{19}NO_2$-SSe 381.030171, found 381.032655.

25: yield: 61%; ^{1}H NMR (200 MHz, $CDCl_3$) δ 00−0.10 (m, 9H), 0.85−0.97 (br s, 13H,), 1.25−1.55 (m, 12H), 1.75−2.05 (m, 2H), 2.40−2.65 (m, 2H), 3.15−3.30 (m, 1H), 4.10 (q, J = 8.1 Hz, 2H), 7.20−7.35 (m, 3H), 7.45−7.57 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.0, 135.6, 127.3, 70.5, 60.2, 43.5, 42.5, 42.1, 37.8, 29.4, 25.9, 25.2, 24.7, 22.5, 18.0, 14.1, −4.1, −4.3; MS *m/e* (relative intensity) 514 (M^+, 4), 457 (22), 244 (100), 171 (30), 157 (20).

32: yield: 65%; ^{1}H NMR (200 MHz, $CDCl_3$) δ −0.05−0.05 (s, 9H), 0.30−0.70 (m, 2H), 1.25 (t, J = 7.3 Hz, 6H), 1.87−2.05 (m, 1H,), 2.10−2.50 (m, 5H), 2.65−2.83 (m, 1H), 2.95−3.05 (m, 1H), 4.2 (q, J = 7.3 Hz, 4H), 7.20−7.35 (m, 3H), 7.45−7.55 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.6, 132.9, 130.4, 128.9, 126.7, 61.3, 58.9, 43.9, 40.6, 38.8, 38.7, 29.1, 16.2, 13.9, −0.1; MS *m/e* (relative intensity) 470 (M^+, 100), 455 (34), 425 (16), 397 (16), 337 (4), 313 (57), 239 (20), 157 (10); HRMS for $C_{22}H_{34}O_4SiSe$ calculated 470.139159, found 470.137444.

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Supporting Information Available: Preparation and characterization details of the compounds **17**, **18**, **24**, and **29** and ^{1}H NMR and ^{13}C NMR spectra of compounds **11**, **19**−**22, 25, 29**, and **32**. This material is available free of charge via the Internet at http://pubs.acs.org.

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