

10.51. Found: C, 89.46; H, 10.77.

**3-Methyl-4,5-exo-epoxybrendane-9-d (23).** Crude 3-methyl-4-brendene-9-d (**22**; 400 mg, 2.96 mmol) was dissolved in methylene chloride (30 mL) and stirred at room temperature with a saturated aqueous solution of sodium bicarbonate (10 mL). MCPBA (850 mg, 4.2 mmol of the active substance) was added, and stirring was continued for an additional 4 h at room temperature. The layers were separated, and the organic one was washed with 1 N NaOH (2 × 20 mL) followed by water (2 × 20 mL) and dried. The solvent was evaporated, and the crude product was purified by column chromatography on neutral alumina (activity II/III). Elution with pentane-ether (3:1) gave epoxide **23** (240 mg, 34% based on the tosylhydrazone of ketone **21**; ≥95% pure by <sup>13</sup>C NMR). The analytical and spectral data for the protio analogue were as follows: mp 73–76 °C; <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 63.6 (d), 59.2 (d), 45.6 (s), 45.2 (d), 41.6 (t), 40.6 (d), 36.7 (d), 35.0 (t), 32.7 (t), 21.0 (q); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 3.4–3.0 (m, 2 H), 2.6–2.1 (m, 2 H), 1.9–0.7 (m, 10 H; sharp signal at δ 1.12); IR (neat) 3010 (sh), 2950 (s), 2860 (s), 1445 (m), 1400 (m), 860 (m), 850 (m) cm<sup>-1</sup>; MS, *m/z* (relative intensity) 150 (M<sup>+</sup>, 5), 122 (9), 106 (32), 93 (82), 92 (24), 91 (25), 84 (100), 81 (34), 80 (84), 79 (47). Anal. Calcd for C<sub>10</sub>H<sub>14</sub>O (150.21): C, 79.95; H, 9.39. Found: C, 80.17; H, 9.68.

**8-Methylene-2-exo-noradamantanol-4-d (25).** A solution of epoxide **23** (160 mg, 1.06 mmol) in dry acetone (2 mL) was stirred with a catalytic amount of trichloroacetic acid (~10 mg) for 30 min at room temperature. Water (30 mL) was added, and the mixture was extracted with chloroform (3 × 20 mL). The extracts were combined and dried. Removal of the solvent af-

forded the crude product, which was purified by column chromatography on neutral alumina (activity II/III) with pentane-ether (2:1) eluent to give pure 8-methylene-2-exo-noradamantanol-4-d, **25** (50 mg, 31%). The <sup>13</sup>C NMR, <sup>1</sup>H NMR, IR, and mass spectra of the protio analogue of **25**, which was obtained by this route, were identical with those of 8-methylene-2-exo-noradamantanol prepared by methyl-Grignard addition to hydroxy ketone **7** followed by dehydration of the resulting methyl diol **8** (Scheme I).

**8-Methylene-2-noradamantanone-4-d (9a)** was obtained in 55% yield by Jones oxidation of **25** through the use of the procedure described for **9**. Deuterium content: 70% *d*<sub>1</sub>, 30% *d*<sub>0</sub> (by MS).

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**Registry No.** 4, 102737-51-9; 7, 88685-73-8; 8, 116026-32-5; 9, 102737-54-2; 9 (tosylhydrazone), 116026-34-7; 9a, 116052-52-9; 10, 116026-50-7; 11, 116026-35-8; 11a, 116026-36-9; 12, 102737-53-1; 12a, 116026-37-0; 18, 32190-81-1; 18 (acid chloride), 33783-95-8; 19, 116026-38-1; 20, 116026-39-2; 21, 116026-42-7; 21 (protio analogue), 116026-40-5; 21 (tosylhydrazone), 116026-44-9; 21 (protio analogue, tosylhydrazone), 116026-43-8; 21a, 116026-41-6; 22, 116026-46-1; 22 (protio analogue), 116026-45-0; 23, 116026-48-3; 23 (protio analogue), 116026-47-2; 25, 116026-49-4; 25 (protio analogue), 116026-33-6.

## The Case Favoring Direct C-Alkylation of Heteroatom-Substituted Enolates

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The alkylation of selenium-stabilized enolates has been shown to proceed by direct alkylation of the enolate carbon atom, rather than by alkylation on selenium and subsequent alkyl group migration to carbon.

Heteroatom-substituted enolates have proven to be useful intermediates for performing many important chemical transformations. For example, depending upon the nature of the hetero group, one can exploit the presence of these heteroatom substituents to (a) enhance reaction regioselectivity, (b) facilitate functional group interconversions, and/or (c) suppress undesired side reactions, such as enolate exchange.<sup>1</sup> This is particularly true when the α-substituent in question is an arylsulfenyl or arylselenenyl group.<sup>2</sup>

From a mechanistic viewpoint these enolates formally belong to that class of anions whose enhanced nucleophilicity has been classified under the general rubric, the "α-effect". Although enolate alkylations with simple

carbon-based electrophiles most likely involve straightforward S<sub>N</sub>2 reactions, the corresponding processes with allylic electrophiles could proceed via a number of alternative pathways. In this regard, one can postulate three general mechanisms. These include: (a) direct allylation on carbon either by an S<sub>N</sub>2 process to give **2** or by an S<sub>N</sub>2' process to give **3** (see pathway A, Scheme I),<sup>3</sup> (b) heteroatom allylation of the enolate to form an ylide, **4**, followed by [2,3]-sigmatropic rearrangement of the allyl group to the α-position (see pathway B), or (c) O-allylation, followed by [3,3]-sigmatropic rearrangement (see pathway C).

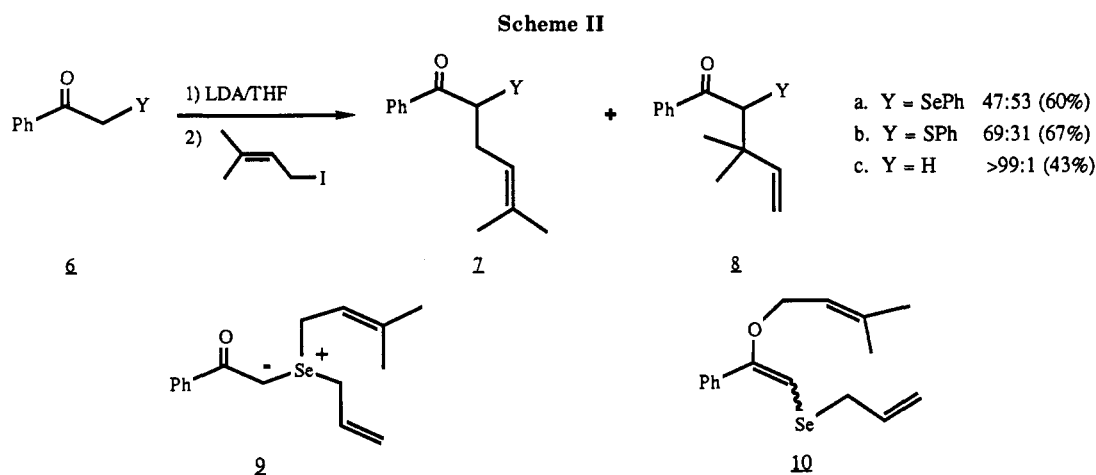
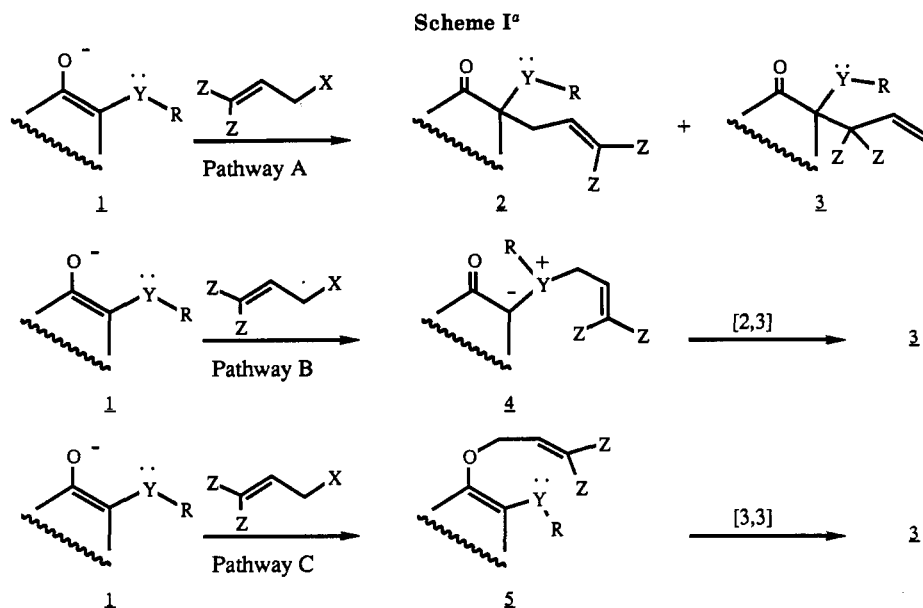
Perhaps the most definitive mechanistic investigation of the allylation of heteroatom-substituted enolates is the elegant study of Reich and Cohen.<sup>4</sup> These workers have reported that enolates derived from seleno- and thio-substituted acetophenones, **6**, give products consistent with pathway B when alkylated with various allyl bromides and iodides. This hypothesis provides an attractive explanation for their observations for the following reasons: (a) assuming ylide formation is faster than direct C-alkylation, it is reasonable that products derived from [2,3]-sigma-

(1) For some papers dealing with this subject, see the following: (a) Reich, H. J.; Shah, S. K. *J. Am. Chem. Soc.* 1975, 97, 3250. (b) Reich, H. J.; Shah, S. K. *J. Am. Chem. Soc.* 1977, 99, 263. (c) Reich, H. J. *J. Org. Chem.* 1975, 40, 2570. (d) Reich, H. J.; Chow, F. *J. Chem. Soc., Chem. Commun.* 1975, 790. (e) Reich, J. J.; Shah, S. K. *J. Org. Chem.* 1977, 42, 1773. (f) Liotta, D.; Zima, G.; Barnum, C. *J. Org. Chem.* 1980, 45, 2737. (g) Liotta, D.; Zima, G.; Barnum, C.; Saindane, M. *Tetrahedron Lett.* 1980, 21, 3643. (h) Liotta, D.; Ensley, H.; Saindane, M.; Barnum, C.; Balkrishnan, P. *Tetrahedron Lett.* 1981, 22, 3043.

(2) For a general description of the synthetic utility of selenium-stabilized enolates, see: *Organoselenium Chemistry*; Liotta, D., Ed.; Wiley-Interscience: New York, 1987.

(3) Note that products derived from S<sub>N</sub>2' reactions formally correspond to those obtained from pathway B.

(4) Reich, H. J.; Cohen, M. L. *J. Am. Chem. Soc.* 1979, 101, 1307.

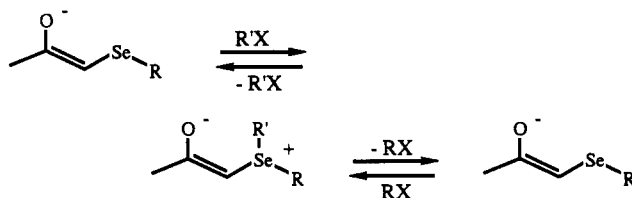


tropic rearrangement of the allyl group (i.e., allylic rearrangement products) should be formed in preference to those derived from competitive [1,3]-shift of the phenyl group; (b) in systems that contain two similar groups capable of migration at the proposed ylide stage (e.g., prenyl and allyl groups), products indicative of migration of both groups were observed; (c) since unsubstituted enolates, such as the one derived from 6c, show no trace of "abnormal" products upon exposure to prenyl halides,  $S_N2'$  displacements should also be unlikely in the corresponding heteroatom-substituted enolates; (d) pathway C can be eliminated, since the independently prepared O-prenylated derivative, 10, required elevated temperatures to achieve [3,3]-rearrangement; and (e) ylide 9 was also prepared independently and shown to rearrange rapidly to its corresponding [2,3]-sigmatropic rearrangement product. Thus, these authors have demonstrated conclusively that pathway C is not operative here, pathway A is unlikely, and if any ylide intermediate is formed, it can rearrange to the observed products. These results notwithstanding, it is our contention that heteroatom alkylations (i.e., pathway B) do not occur in these systems.

### Results and Discussion

In order to independently probe the first step of pathway B, we examined a series of reactions that should generate a putative ylide intermediate possessing alkyl groups of

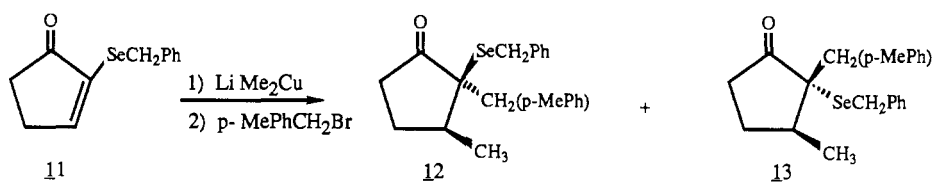
nearly identical reactivity but that are incapable of undergoing a [2,3]-sigmatropic rearrangement.<sup>5,6</sup> Fast, reversible ylide formation, followed by slower, but irreversible C-alkylation, should result in alkyl-group scrambling. The same should be true if the mechanism instead involved irreversible ylide formation, followed by [1,3]-sigmatropic rearrangement (vide infra).



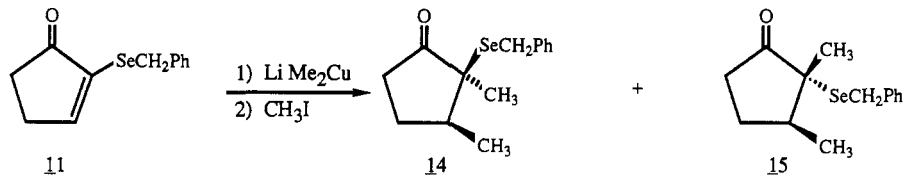
(5) (a) The substrates that were examined in this study include various  $\alpha$ -selenated cyclopentanone and  $\alpha$ -tetralone moieties, which were prepared by using the "enolate-selenolate" methodology developed in our laboratories. See ref 1g,h. (b) The method for synthesizing enone 11 involves the addition of selenium metal to an  $\alpha$ -ketovinyl anion equivalent at  $-78^\circ\text{C}$ . The Se is allowed to react with the anion for 30 min before alkyl halide addition, and the resulting reaction mixture is allowed to warm to room temperature and stir overnight. For a reference on  $\alpha$ -ketovinyl anion equivalent methodology, see: Smith, A. B.; Branca, S. J. *Am. Chem. Soc.* 1978, 100, 7767.

(6) Product isomer ratios were determined by  $^1\text{H}$  NMR analysis. In all cases product identification was further corroborated by analysis of  $^1\text{H}$  NMR and mass spectral data of the products derived from oxidative elimination or deselenation of the selenium.

## Scheme III

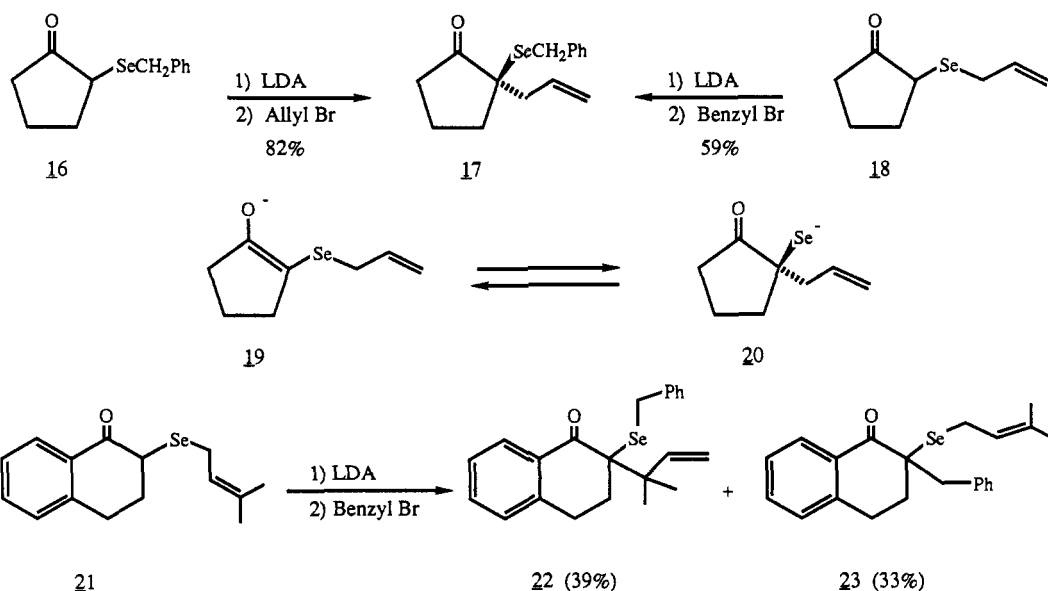


5:1 (73%)



4:1 (96%)

## Scheme IV



In the first experiment, 2-(benzylselenenyl)cyclopentanone, 11, was treated with lithium dimethylcuprate, followed by alkylation of the resulting enolate with 1 equiv of *p*-methylbenzyl bromide. Under these conditions, no scrambling of the benzyl and *p*-methylbenzyl groups was observed. Therefore, unless allyl halides are vastly different than benzyl halides in their preferences for alkylating selenium-stabilized enolates, this result is only compatible with a direct C-alkylation mechanism, since even a reversible alkylation of selenium should produce scrambling. As a final test of this reversibility phenomenon, we examined the reaction of 11 with lithium dimethylcuprate, followed by methyl iodide (Scheme III). If an ylide intermediate had been produced via a fast, reversible alkylation on selenium, some C-benylation would be expected; however, none was observed.

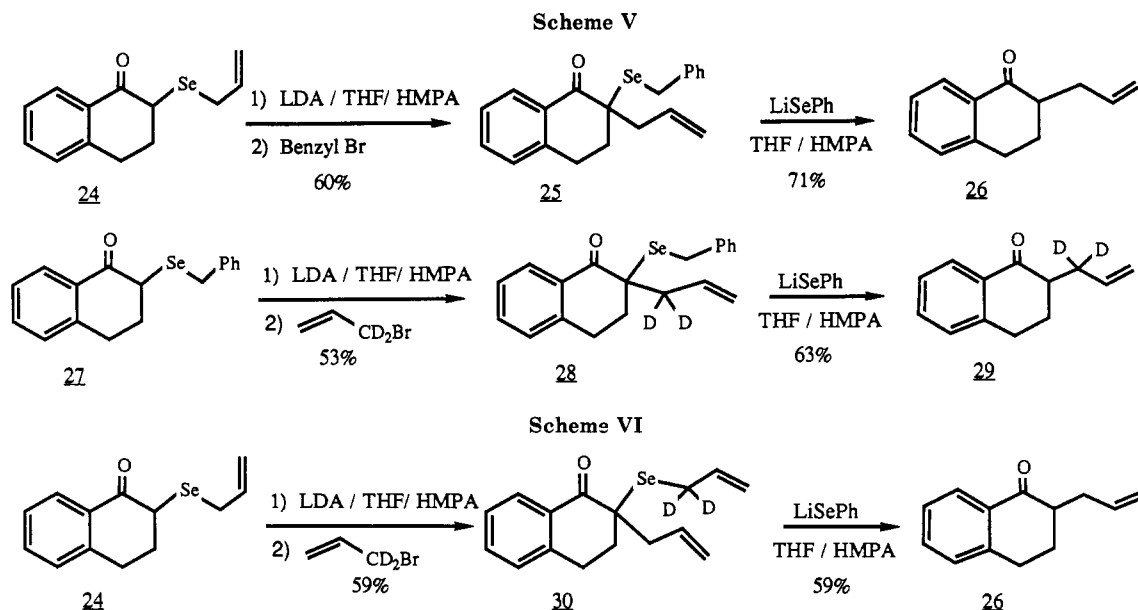
In order to be sure that the method of enolate generation did not affect the outcome of our studies, we have also generated selenium-stabilized enolates by deprotonation of  $\alpha$ -alkylselenenyl ketones. For example, alkylation of 2-(benzylselenenyl)cyclopentanone, 16, with lithium diisopropylamide/allyl bromide/HMPA resulted in the formation of the C-allylated material 17 (Scheme IV). While not provocative on its own, this observation takes on greater significance when it is considered in tandem

with another result, i.e., alkylation of 2-(allylselenenyl)cyclopentanone, 18, with lithium diisopropylamide/benzyl bromide/HMPA also leads to the exclusive formation of 17. These results can be explained in two different ways. One can invoke the mechanism described by pathway B. Alternatively, the observed product could also arise from [2,3]-sigmatropic rearrangement of enolate 19 to form selenolate anion 20 (Scheme IV), which then undergoes benzylation at selenium.<sup>7,8</sup> Similar rationales could also be used to explain the products obtained in the benzylation of 21, except that in this case the equilibrium is shifted further toward the enolate for steric reasons (Scheme IV).

In an effort to differentiate between these two possibilities, we have performed three experiments, which unequivocally demonstrate which of the pathways is operative. Benzylation of 24, followed by reductive deselenation with lithium phenylselenide, yields 26 (Scheme V). As before, this material could have been formed by [2,3]-sigmatropic rearrangement at either the ylide or enolate stages. However, alkylation of 27 with regioselectively

(7) Baldwin, J. E.; Tzodikov, N. R. *J. Org. Chem.* 1977, 42, 1878.

(8) In footnote 7 of ref 4, it is stated that on the basis of control experiments, [2,3]-sigmatropic rearrangements of enolates were ruled out. However, no details of the control experiments were reported.

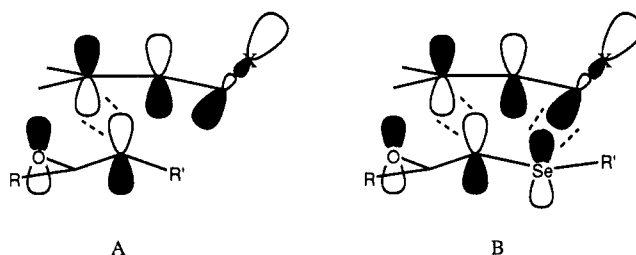


labeled allyl bromide- $d_2$  gave a product whose formation is most readily understood in terms of a direct C-alkylation (Scheme V). Moreover, alkylation of 24 with the same deuteriated allyl bromide leads to a product whose formation can only be explained via a [2,3]-rearrangement of the initially formed enolate, followed by  $S_N2'$  reaction of the resulting selenolate with the deuteriated electrophile (Scheme VI).

Having demonstrated that heteroatom allylations of selenium-stabilized enolates are not generally operative processes and that virtually all of the "abnormal" allylation results can be understood in terms of [2,3]-sigmatropic rearrangements of selenium-substituted enolates, we must either present an alternate rationale to explain the conversions of 6a (and 6b) to 7a and 8a (7b and 8b) or accept that fact that heteroatom allylation occurs in this one case. While the latter possibility can not be ruled out, we find it to be intellectually dissatisfying. Instead, we propose that the large amount of "abnormal" product (i.e., 8a and 8b) observed in these reactions results from an enhanced propensity of heteroatom-substituted enolates to undergo  $S_N2'$  reactions. This can be best understood by examining the appropriate frontier orbitals of the enolate and allyl halide (see Figure 1).

In reactions involving unsubstituted enolates, the major stabilizing frontier orbital interaction in the  $S_N2'$  reaction is the one between the enolate HOMO and the allyl halide LUMO. However, in reactions involving heteroatom-substituted enolates, additional stabilization can be gained from secondary orbital interaction between the heteroatom and carbon-halogen components of their HOMO and LUMO, respectively. Furthermore, it follows that as the basis energy of the heteroatom lone pair orbital increases, so too would the magnitude of the stabilization. Since selenium lone pairs generally exhibit lower ionization potentials than their corresponding sulfur analogues,<sup>9</sup> it follows that selenium-stabilized enolates should give larger amounts of products derived from  $S_N2'$  reaction.

In summary, we have demonstrated that heteroatom-allylations of selenium-stabilized enolates are not operative processes. In addition, we suggest that heteroatom-substituted enolates are more likely to undergo  $S_N2'$  reaction



**Figure 1.** (A) Frontier orbital interactions in  $S_N2'$  reactions of unsubstituted enolates and allyl halides. (B) Frontier orbital interactions in  $S_N2'$  reactions of selenium-substituted enolates and allyl halides.

than their unsubstituted counterparts.

### Experimental Section

**General Methods.**  $^1H$  NMR spectra were recorded on a Nicolet 360-MHz spectrometer and are reported in ppm with  $CDCl_3$  (7.26 ppm) as internal standard.  $^{13}C$  NMR were obtained on a General Electric QE-300 instrument and are reported in ppm with  $CDCl_3$  ( $\tau$  at 77.00 ppm) as internal standard. IR spectra are reported in reciprocal centimeters ( $cm^{-1}$ ) and were obtained on a Perkin-Elmer 1430 ratio recording spectrophotometer. Mass spectra were obtained at 70 eV on a VG 70-S Nier Johnson Mass Spectrometer. All solvents were distilled and dried with the usual desiccants. The purity of the various synthetic intermediates was assessed by evaluation of their spectral (IR, MS, and NMR) and chromatographic (TLC) data. Combustion analyses were performed by Atlanta Microlab, Inc.

**A Representative Procedure for the Conversion of Ketones to Their Corresponding  $\alpha$ -Alkyl Selenenyl Ketones.** This procedure is illustrated below for the conversion of cyclopentanone to 18. To a 500-mL three-neck flask containing THF (250 mL) and a few crystals of  $\alpha,\alpha'$ -dipyridyl, under  $N_2$ , was added (5.82 g, 57.6 mmol) diisopropylamine. The solution was cooled to  $-78^\circ C$  (34.9 mL, 1.65 M, 57.6 mmol)  $n-BuLi$  was added, and LDA was allowed to form for 10 min before cyclopentanone (4.03g, 48 mmol) was added. This solution was stirred for 1 h, HMPA (26 mL, 48 mmol) was added and stirred for 5 min, and ground selenium (3.86 g, 48 mmol) was introduced and warmed to  $-20^\circ C$ . After 1 h of stirring at approximately  $-20^\circ C$ , including a brief warming period to  $-10^\circ C$ , allyl bromide (5.82 g, 48 mmol) was added and stirred for 5 min. The reaction was quenched with saturated  $NH_4Cl$  (10 mL), diluted with ether (100 mL), and washed twice with 10% HCl (25 mL) and twice with water (25 mL). The organic layer was separated, dried with  $MgSO_4$ , and rotovaped. Chromatography (silica gel,  $Et_2O/Hexane$ ) afforded 18 (5.62 g, 58%):  $^1H$  NMR ( $CDCl_3$ )  $\delta$  5.85 (m, 1), 5.10 (dd, 2),

(9) Baker, A. D.; Armen, G. H.; Guang-di, Y.; Liotta, D.; Flannagan, N.; Barnum, C.; Saindane, M.; Zima, G.; Grossman, J. *J. Org. Chem.* 1981, 46, 4172.

3.35 (m, 3, SeCH and SeCH<sub>2</sub>), 2.10 (m, 6); IR (CHCl<sub>3</sub>) 1729, 1220, 750, 670 cm<sup>-1</sup>; mass spectrum, *m/e* 204.

**A Representative Procedure for the Alkylation of  $\alpha$ -Alkyl Selenenyl Ketones.** This procedure is illustrated below for the conversion of 18 to give 17. To a 100-mL three-neck flask containing THF (50 mL) and a few crystals of  $\alpha,\alpha'$ -dipyridyl, under N<sub>2</sub>, was added diisopropylamine (0.30 g, 3 mmol). The solution was cooled to -78 °C, *n*-BuLi (1.67 mL, 1.65 M, 3 mmol) was added, and LDA was allowed to form for 10 min before 18 (0.50 g, 2.5 mmol) was added. This solution was stirred for 35 min, HMPA (1.3 mL, 7.5 mmol) was added and stirred for 5 min, and benzyl bromide (0.42 g, 2.5 mmol) was introduced and allowed to stir at ambient temperature for 17 h. The reaction was quenched with 2 mL of saturated NH<sub>4</sub>Cl, diluted with ether (100 mL), and washed twice with 10% HCl (20 mL) and twice with water (20 mL). The organic layer was separated, dried with MgSO<sub>4</sub>, and rotovaped. Column chromatography (silica gel, Et<sub>2</sub>O/hexane) and HPLC afforded pure 17 (0.43 g, 59%): <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.27 (m, 5), 5.75 (m, 1), 5.10 (dd, 2), 3.80 (d, 2, *J* = 15.1 Hz, SeCH<sub>2</sub>), 2.55 (dd, 2, allyl), 1.95 (m, 6); IR (CHCl<sub>3</sub>) 1715, 1220, 750, 670 cm<sup>-1</sup>; mass spectrum, *m/e* 294.

**A Representative Procedure for the Deselenation of  $\alpha$ -Alkyl Selenenyl Ketones.** This procedure is illustrated below for the conversion of 28 to 29. To a 50-mL three-neck flask containing THF (25 mL) under N<sub>2</sub> was added finely ground selenium (0.064 g, 0.6 mmol) the solution was cooled to -78 °C, and PhLi (0.35 mL, 1.7M, 0.6 mmol) and HMPA (0.43 g, 2.4 mmol) were added sequentially and stirred for 1 h. To the reaction mixture was then added a solution of 28 (150 mg, 0.4 mmol) in THF (3 mL). The reaction mixture was then allowed to stir at ambient temperature for 1 h. The reaction was quenched with saturated NH<sub>4</sub>Cl (2 mL), diluted with ether (50 mL), and extracted three times with water and once with saturated NaCl. The organic layer was separated, dried with MgSO<sub>4</sub>, and rotovaped. Chromatotron (silica gel, Et<sub>2</sub>O/hexane) purification afforded pure 29 (0.05 g, 63%): <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  8.16 (d, *J* = 7.6 Hz, 1), 7.33 (m, 3), 5.83 (m, 1), 5.10 (m, 2), 3.02 (m, 2), 2.54 (m, 1), 2.23 (m, 1), 1.87 (m, 1); mass spectrum, *m/e* calcd, 188.1170, found 188.1157.

**Preparation of [1,1-<sup>2</sup>H<sub>2</sub>]Allyl Bromide.** To a 250-mL three-neck flask, containing Et<sub>2</sub>O (150 mL) under N<sub>2</sub>, was added lithium aluminum deuteride (5.0 g, 119 mmol). The solution was cooled to 0 °C, and acryloyl chloride (20.46 g, 226 mmol) was added slowly via syringe. The reaction was maintained at 0 °C for 1 h. The reaction mixture was quenched with 10% NaOH solution (20 mL) and extracted five times with Et<sub>2</sub>O. The crude product was placed in a 500-mL three-neck flask equipped with a mechanical stirrer under N<sub>2</sub>. To the flask was added Et<sub>2</sub>O (250 mL), and the solution was cooled to 0 °C. Under N<sub>2</sub> was added CBr<sub>4</sub> (75g, 226 mmole). To the reaction mixture was slowly added triphenylphosphine (59.2 g, 1.9 equiv) under N<sub>2</sub> and the reaction mixture was allowed to sit at ambient temperature overnight. The crude reaction mixture was filtered, and the product was distilled to yield the pure product, [1,1-<sup>2</sup>H<sub>2</sub>]allyl bromide (2.0g, 7%): bp 60–90 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  5.98 (m, 1), 5.43 (m, 2).

**Spectral and Analytical Data.** 11: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.3 (m, 5), 4.0 (m, 2), 2.4 (m, 5).

12: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.2 (m, 9), 3.8 (d, 2, *J* = 3 Hz), 3.6 (d, 1, *J* = 10 Hz), 3.1 (d, 1, *J* = 15 Hz), 2.5 (m, 2), 2.2 (m, 5), 1.5 (m, 1), 1.0 (d, 3, *J* = 6 Hz). Anal. Calcd for C<sub>21</sub>H<sub>24</sub>SeO: C, 67.92; H, 6.51. Found: C, 67.67; H, 6.43.

13: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.2 (m, 9), 3.7 (d, 2, *J* = 3 Hz), 3.2 (d, 1, *J* = 15 Hz), 2.9 (d, 1, *J* = 15 Hz), 2.2 (m, 7), 1.5 (m, 1) 1.0 (d,

3, *J* = 6 Hz). Anal. Calcd for C<sub>21</sub>H<sub>24</sub>SeO: C, 67.92; H, 6.51. Found: C, 67.81; H, 6.32.

14: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.3 (m, 5), 3.8 (d, 2, *J* = 3 Hz), 2.2 (m, 4), 1.5 (m, 1), 1.2 (s, 3), 1.0 (d, 3, *J* = 6 Hz). Anal. Calcd for C<sub>14</sub>H<sub>18</sub>SeO: C, 59.79; H, 6.45. Found: C, 59.40; H, 6.63.

15: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.3 (m, 5), 3.8 (d, 2, *J* = 3 Hz), 2.2 (m, 2), 1.8 (m, 2), 1.5 (m, 1), 1.2 (s, 3), 1.0 (d, 3, *J* = 6 Hz). Anal. Calcd for C<sub>14</sub>H<sub>18</sub>SeO: C, 59.79; H, 6.45. Found: C, 59.51; H, 6.83.

16: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.3 (m, 5), 3.9 (m, 2), 3.3 (m, 1), 2.0 (m, 6); IR 1729, 1220, 750, 670 cm<sup>-1</sup>; mass spectrum, *m/e* 254.

17: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.27 (m, 5), 5.75 (m, 1), 5.1 (m, 2), 3.8 (t, 2), 2.55 (m, 2, allyl), 1.95 (m, 6); IR 1715, 1220, 750, 670 cm<sup>-1</sup>; mass spectrum, *m/e* 294. Anal. Calcd for C<sub>25</sub>H<sub>18</sub>SeO: C, 61.43; H, 6.19. Found: C, 61.23; H, 6.60.

18: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  5.85 (m, 1), 5.1 (m, 2), 3.35 (m, 3), 2.1 (m, 6); IR 1729, 1220, 750, 670 cm<sup>-1</sup>; mass spectrum, *m/e* 204.

21: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  8.10 (d, *J* = 7.6 Hz, 1), 7.4 (m, 3), 5.35 (t, *J* = 8.9 Hz, 1), 3.85 (m, 1), 3.5 (dd, *J* = 8.9, 2.6 Hz, 2), 3.0 (m, 2), 2.4 (m, 2), 1.72 (s, 3), 1.7 (s, 3); IR 1670, 1220, 750 670 cm<sup>-1</sup>; mass spectrum, *m/e* 294.

22: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  8.13 (d, *J* = 7.6 Hz), 7.1–7.5 (m, 8), 6.30 (m, 1), 5.05 (m, 2), 4.00 (d, *J* = 10.8 Hz, 1), 3.55 (d, *J* = 10.8 Hz, 1), 3.00 (m, 2), 2.15 (m, 2), 1.40 (d, *J* = 9.6 Hz, 6); IR (CHCl<sub>3</sub>) 1665, 1220, 750, 670 cm<sup>-1</sup>; mass spectrum, *m/e* 384. Anal. Calcd for C<sub>22</sub>H<sub>24</sub>SeO: C, 68.92; H, 6.31. Found: C, 68.67; H, 6.01.

23: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  8.12 (d, *J* = 7.6 Hz, 1), 7.1–7.4 (m, 8), 5.25 (t, 1), 3.80 (d, 2), 3.20 (d, *J* = 13.6 Hz, 2), 3.00 (m, 2), 2.10 (m, 2), 1.65 (2 br s, 6); IR (CHCl<sub>3</sub>) 1670, 1220, 750, 670 cm<sup>-1</sup>; mass spectrum, *m/e* 384. Anal. Calcd for C<sub>22</sub>H<sub>24</sub>SeO: C, 68.92; H, 6.31. Found: C, 68.74; H, 6.11.

24: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  8.16 (d, *J* = 7.6 Hz, 1), 7.33 (m, 3), 5.83 (m, 1), 5.26 (m, 1), 5.12 (m, 1), 3.84 (m, 1), 3.45 (m, 1), 3.19 (m, 2), 2.87 (m, 1), 2.55 (m, 1), 2.13 (m, 1); mass spectrum, *m/e* calcd 266.0210, found 266.0197.

25: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  8.20 (d, *J* = 7.6 Hz, 1), 7.28 (m, 8), 5.83 (m, 1), 5.12 (m, 2), 3.81 (m, 2), 3.21 (m, 1), 2.86 (m, 3), 2.25 (m, 2); mass spectrum, *m/e* calcd 356.0679, found 356.0676. Anal. Calcd for C<sub>20</sub>H<sub>20</sub>SeO: C, 67.60; H, 5.67. Found: C, 67.67; H, 6.02.

26: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  8.05 (d, *J* = 7.6 Hz, 1), 7.39 (m, 3), 5.83 (m, 1), 5.12 (m, 2), 2.99 (m, 2), 2.71 (m, 1), 2.49 (m, 1), 2.25 (m, 2), 1.85 (m, 1); mass spectrum, *m/e* calcd 186.1044, found 186.1042.

27: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  8.16 (d, *J* = 7.6 Hz, 1), 7.33 (m, 3), 3.92 (m, 2), 3.80 (m, 1), 3.12 (m, 1), 2.82 (m, 1), 2.50 (m, 1), 2.24 (m, 1); mass spectrum, *m/e* calcd 316.0366, found 316.0288.

28: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  8.16 (d, *J* = 7.6 Hz, 1), 7.33 (m, 3), 5.83 (m, 1), 5.14 (m, 2), 3.78 (m, 2), 3.15 (m, 1), 2.81 (m, 1), 2.28 (m, 2).

29: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  8.16 (d, *J* = 7.6 Hz, 1), 7.33 (m, 3), 5.83 (m, 1), 5.10 (m, 2), 3.02 (m, 2), 2.54 (m, 1), 2.23 (m, 1), 1.87 (m, 1); mass spectrum, *m/e* calcd 188.1170, found 188.1157.

30: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  8.16 (d, *J* = 7.6 Hz, 1), 7.33 (m, 3), 5.83 (m, 2), 5.10 (m, 4), 3.24 (m, 2), 2.81 (m, 2), 2.25 (m, 2); mass spectrum, *m/e* calcd 308.0648, found 308.0665.

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