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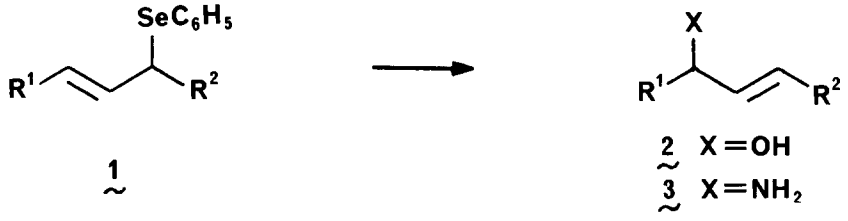
SYNTHESIS OF PROTECTED ALLYLIC AMINES FROM ALLYLIC PHENYL SELENIDES: IMPROVED CONDITIONS FOR THE CHLORAMINE T OXIDATION OF ALLYLIC PHENYL SELENIDES

John E. Pankhauser,[1a] Richard M. Peevey,[1b] and Paul B. Hopkins*[1c]
Department of Chemistry, University of Washington, Seattle, Washington 98195

Summary: Anhydrous chloramine T in methanol is a highly effective reagent for the conversion of allylic phenyl selenides to the corresponding rearranged N-allylic-*p*-toluenesulfonamides. The reaction presumably proceeds via an allylic selenimide intermediate which undergoes [2,3]-sigmatropic rearrangement.

The oxidative conversion of allylic selenides to allylic alcohols (1->2) is a useful synthetic transformation[2] which proceeds with both high regio- and stereospecificity.[3] In sharp contrast, the mechanistically analogous oxidative conversion of allylic selenides to allylic amines (1->3), or derivatives thereof, has remained essentially unexplored,[4] despite the potential synthetic utility of such a procedure.



1

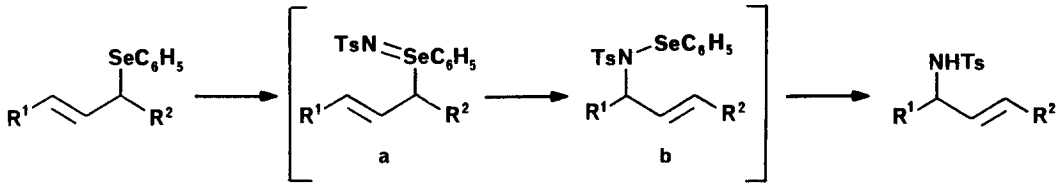
2 X=OH

3 X=NH_2

In connection with a synthetic project currently underway, we have investigated a variety of experimental conditions designed to effect the conversion of allylic phenyl selenides to protected allylic amines.[5] We report at this time that this conversion can be efficiently carried out using 2.0 equivalents of anhydrous chloramine T[6] in methanol at 25°. This reaction presumably proceeds by way of the selenimide[7] intermediate *a* which undergoes [2,3]-sigmatropic rearrangement[8] to selenenamide *b* followed by methanolysis to afford the observed product, an N-tosyl allylic amine. The accompanying table illustrates several examples of this preparation of allylic sulfonamides[9]. The indicated yields of purified sulfonamides were obtained by filtration of the crude reaction mixtures through Celite followed by direct column chromatography on silica gel. The conversion of the isomeric allylic selenides in entries 2 and 7 to the indicated isomeric sulfonamides clearly supports the proposed [2,3]-sigmatropic rearrangement mechanism. The reductive cleavage of allylic sulfonamides to allylic amines using

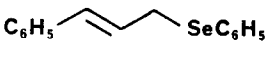
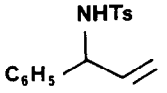
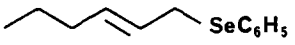
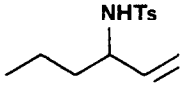
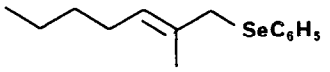
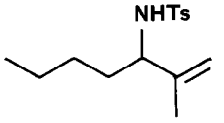
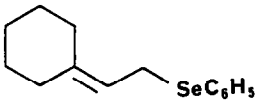
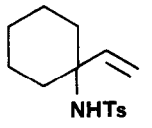
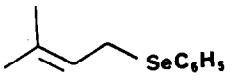
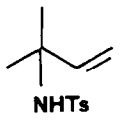
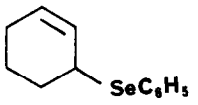
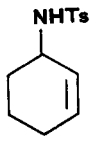
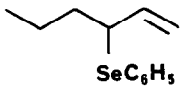
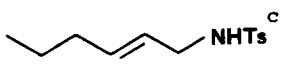
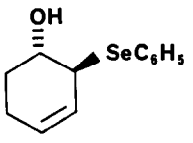
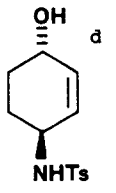
sodium-naphthalene has been previously achieved,[10] and in combination with the present reaction constitutes a two step synthesis of allylic amines from allylic selenides (1->3).

Several experimental observations made during these studies are noteworthy. The use of methanol as reaction solvent appears to be critical: Significantly less clean reaction mixtures resulted when reactions were conducted in *tert*-butanol, methylene chloride, or dimethylformamide. This may reflect the ability of methanol to serve efficiently as a nucleophile in the cleavage of the N-Se bond in the rearrangement product *b*. Additionally, despite TLC (SiO_2) evidence suggesting complete comsumption of the starting selenide after minutes (even at -78°), the indicated yields were obtained only after stirring 24 h at 25°. Shorter reaction times provided decreased yields. This may again reflect the need for methanolysis of intermediate *b*. The use of *anhydrous* chloramine T is central to the efficiency of the transformation: In the case of entry 2, a yield of 40% was obtained using *ca.* 2 equiv. of commercial chloramine T *hydrate* under otherwise identical conditions. Finally, TLC indicates that a minimum of 2 equiv. of anhydrous chloramine T is required for complete consumption of starting material while a large excess (5.0 equiv.) appears to be deleterious.



The ready availability of allylic phenyl selenides by direct displacement of activated allylic alcohol derivatives with the highly nucleophilic phenyl selenide anion,[11] by alkylation of allylic phenyl selenide anions,[12] and, most recently, by Wittig homologation of α-phenylseleno aldehydes[13] enhances the utility of the process described herein. Furthermore, the reaction conditions are sufficiently mild that a variety of functional groups are expected to be compatible with this transformation. Further studies to explore the stereochemical details of this process and its application in the preparation of more complex molecules will be reported in due course.[15]

Representative Procedure: To a suspension of 381 mg (1.67 mmol) of anhydrous chloramine T in 2.0 mL of methanol under argon at 25° was added 200 mg (0.836 mmol) of *trans*-1-phenylseleno-2-hexene. Within seconds, an extensive white precipitate formed. The resulting suspension was stirred 24 h at 25°, filtered through a plug of Celite 503, and the filter cake was rinsed with 2.0 mL of ethyl acetate. The combined filtrates were concentrated *in vacuo* and chromatographed on silica gel (15% ethyl acetate-hexanes as eluent) to provide 186 mg (88%) of 3-(*p*-toluenesulfonylamino)-1-hexene as a colorless oil, PMR (500 MHz, $CDCl_3$): δ 7.83 (2H, d, J=8); 7.28 (2H, d, J=8); 5.54 (1H, ddd, J=17.1, 10.5, 6.5); 4.98 (1H, d, J=17.1); 4.94 (1H, d, J=10.5); 4.78 (1H, broad); 3.77 (1H, m); 2.43 (3H, s); 1.44 (2H, m); 1.27 (2H, m); 0.93 (3H, t, J=7.6); IR ($CHCl_3$): 3380 (NH), 3270 (NH), 1600 (ArH), 1500 (ArH), 1335 (SO_2), 1160 (SO_2), 1100, 930, 810, 650 cm^{-1}; MS (ei) m/e 253 (M^+), 226 ($M^+-C_2H_3$), 210 ($M^+-C_3H_7$), 155 p-$CH_3C_6H_4SO_2$); Exact mass calc'd for $C_{13}H_{19}NO_2S$: 253.114; Found: 253.112.

Entry	Allylic Selenide[a]	Allylic Sulfonamide[b]	Yield[e]
1			84
2			88
3			84
4			76
5			88
6			74
7			74[f]
8			91

a. Selenides in entries 1 through 6 were prepared from allylic mesylates or halides and sodium phenyl selenide in ethanol at 25°.[3b] The substitution pattern was in all cases clearly evident from the PMR spectrum. The entry 7 selenide was prepared according to Reich[12] and was of *ca.* 80% purity; the entry 8 selenide was derived from 3,4-epoxycyclohexene and sodium phenyl selenide.[14] b. Ts = *p*-toluenesulfonyl. c. J_{trans} = 15 Hz; *cis* isomer not detected by PMR. d. The indicated *trans* stereochemistry of the substituents is mechanistically implied but has not been rigorously demonstrated. e. Yields represent isolated, chromatographically homogeneous material.[9] f. Yield based on allylic selenide in starting material (see a above).

References and Endnotes

1. (a) Undergraduate Research Associate; (b) Graduate Research Associate; (c) Recipient of a Dreyfus Grant for Newly Appointed Faculty in Chemistry, 1982-1987.

2. Sharpless, K. B.; Lauer, R. F. J. Am. Chem. Soc. 1972, 94, 7154.

3. (a) H. Reich in "Oxidation in Organic Chemistry," Pt. C, W. S. Trahanovsky, Ed. (New York: Academic Press, 1978), pp. 102-107; (b) Clive, D. J. Tetrahedron 1978, 34, 1049.

4. Sharpless has communicated a single example of this reaction: Sharpless, K. B.; Hori, T. J. Org. Chem. 1979, 44, 4208. In our experience, the experimental conditions described herein have provided considerably cleaner reaction mixtures than those described in the original report.

5. For other syntheses of protected allylic amines with allylic rearrangement, see Overman, L. J. Am. Chem. Soc. 1976, 98, 2901 and references cited therein.

6. Dried as described by Sharpless: Sharpless, K. B.; Hori, T.; Truesdale, L. K.; Dietrich, C. O. J. Am. Chem. Soc. 1976, 98, 269. CAUTION: An explosion of anhydrous chloramine T has been reported: Chem. Eng. News, p. 56, Dec. 5, 1977. Review: Campbell, M. M.; Johnson, G. Chem. Rev. 1978, 78, 65.

7. Stable selenimides have been previously prepared: (a) Hellwinckel, D.; Fahbach, G. Justus Liebigs Ann. Chem. 1968, 715, 68; (b) Derkach, N. Y.; Lyapina, T. V.; Pasmurtseva, N. A. Zh. Org. Khim. 1974, 10, 807 (Chem. Abstr. 1974, 81, 25294j); (c) Tamagaki, S.; Oae, S.; Sakaki, K. Tetrahedron Lett. 1975, 649; (d) David, F. A.; Billmers, J. M.; Stringer, O. D. Tetrahedron Lett. 1983, 24, 3191.

8. For related [2,3]-sigmatropic rearrangements of imido selenium compounds, see: (a) Sharpless, K. B.; Singer, S. P. J. Org. Chem. 1976, 41, 2506; (b) Sharpless, K. B.; Hori, T.; Truesdale, L. K.; Kietrich, C. O. J. Am. Chem. Soc. 1976, 98, 269. For analogous imido sulfur rearrangements, see: (a) Ash, A. S. F.; Challenger, F.; Greenwood, D. J. Chem. Soc. 1951, 1877; (b) Ash, A. S. F.; Challenger, F. J. Chem. Soc. 1952, 2792; (c) Briscoe, P. A.; Challenger, F.; Duckworth, P. S. J. Chem. Soc. 1956, 1755; (d) Tamura, Y.; Matsushimi, H.; Minamikawa, J.; Iked, M.; Sumoto, K. Tetrahedron 1975, 31, 3035.

9. All of the allylic sulfonamides exhibited IR, NMR, MS, and exact mass data in accord with the indicated structures. The entry 1 and 6 sulfonamides were compared with authentic samples.

10. Ji, S.; Gortler, L. B.; Waring, A.; Battisti, I.; Bank, S.; Closson, W. D.; Wriede, P. J. Am. Chem. Soc. 1967, 89, 5311.

11. See reference 3b.

12. Reich, H. J. J. Org. Chem. 1975, 40, 2570.

13. Di Giamberardino, T.; Halazy, S.; Dumont, W.; Krief, A. Tetrahedron Lett. 1983, 24, 3413.

14. Crandall, J. K.; Banks, D. B.; Colyer, R. A.; Watkins, R. J.; Arrington, J. P. J. Org. Chem. 1968, 33, 423.

15. This research was generously supported by the University of Washington Graduate School Research Fund and the Dreyfus Foundation. We thank Professor Stanley Raucher for several helpful discussions and Bradley J. Tenge for technical assistance.

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