## TRANSFORMATION OF $\alpha$ -PHENYLSELENOKETONES TO ALLYLIC SELENIDES VIA MIGRATION OF THE PHENYLSELENO GROUP

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Abstract  $\alpha$ -Phenylselenoketones were readily converted to the allylic selenides by treatment with trimethylsilylmethyllithium and subsequent reaction with tin(II)chloride via a facile migration of the phenylseleno group in course of the reaction

 $\alpha$ -Phenylselenoketones are readily available and useful intermediates for the preparation of  $\alpha,\beta$ -unsaturated ketones or allylic alcohols.<sup>1</sup> We now report here that Peterson's olefination<sup>2</sup> of  $\alpha$ -phenylselenoketones via acidcatalyzed dehydroxysilylation gives unexpectedly the primary allylic selenides due to the phenylseleno migration



The  $\alpha$ -phenylselenoketone <u>1</u> was allowed to react with trimethylsilylmethyllithium (ca. 0 5-0.8 N in pentane-ether) at -78 °C in Et<sub>2</sub>O and the resulting mixture was quenched with water at -78 °C to give 2-hydroxy-3-trimethylsilylpropyl selenide <u>2</u> The crude <u>2</u> was directly subjected to treatment with a catalytic amount of tin(II) chloride (ca 10-20 mol%) in CH<sub>2</sub>Cl<sub>2</sub> at 0 °C for 2-3 hr to form the allylic selenide <u>3</u> (Table 1). As shown in entry 2-8, the phenylseleno group is situated on the primary position of the corresponding allylic selenide. As further findings, phenylselenoacetone- $d_5 - 4$  gave a mixture of isomers  $5 \text{ and } 6 (65\%, 56 = 11)^3$  The scrambling can be attributed to absence of the substitutional preference between two allylic sites. On the other hand, olefination of alcohol 7 under basic condition (1 equiv. of t-BuOK, THF, r.t, 3 hr.) gave only 5 in 69% yield as a normal dehydroxysilylation product via a syn-elimination.<sup>4</sup> Treatment of pure 5 under the acidic condition previously employed (cat  $\text{SnCl}_2$ ,  $\text{CH}_2\text{Cl}_2$ , a little amount of MeOH as a proton sourse, 0 °C, 2 hr), however, did never afford the phenylseleno migration product 6



a): Me3SiCH<sub>2</sub>Li, -78°, ii H<sub>2</sub>O b) cat SnCl<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>(MeOH), O°, 2 hr c) <sup>t</sup>BuOK, THF, r t , 2 hr

Moreover, no 1,3-migration of the phenylseleno group was observed even in the case of a secondary allylic selenides,  $PhSeCH(CH_3)CH=CH_2$ , under the above acidic condition Consequently, these observation can be interpreted as follows The acid catalyzed dehydroxylation of 2-hydroxy-3-trimethylsilylpropyl selenides 2 gives initially a cationic species 1, which readily afford the primary allylic selenides 3, which is thermodynamically more stable, by way of the simultaneous phenylseleno migration in course of the desilylation.<sup>5</sup>



Entry	Ketone <u>1</u> <sup>a</sup>	Alcohol <u>2</u> yıeld [%] <sup>b</sup>	Allylıc Selenide <u>3</u> yıeld(%) <sup>C</sup> [%] <sup>d</sup>	
1	PhSe	[68]	PhSe	(40) [96]
2	PhSe 0	[86]	PhSe nc4+	1 <sub>9</sub> (62)[85]
3	PhSe $C_2H_5$	[82]	PhSe CH <sub>3</sub>	(55)[95]
4	PhSe Calle		PhSe C <sub>2</sub> H	5 (66)
5	PhSe		PhSe CH <sub>2</sub> P	h (61)
6	Ph Ph PhSe 0		PhSe CH <sub>3</sub>	(87)
7	PhSe 0	[58]	PhSe CH3	3 [54] <sup>H</sup> 7
8	CH3 ''C3H7 0 PhSe	[51]	PhSe	, (33)[82]

Table 1. Transformation of  $\alpha$ -Phenylselenoketones to Allylic Selenides

<sup>a</sup> ca. 1-2 mmol scale. <sup>b</sup> Isolated yield. Small amounts of  $PhSeCH_2SiMe_3$  (ca. 10%) were obtained. <sup>c</sup> Isolated yield based on <u>1</u> via the crude alcohols <u>2</u>. <sup>d</sup> Isolated yield based on the purified <u>2</u>. All products <u>3</u> were contaminated by small amounts of PhSeSePh

Thus we have found a new transformation of  $\alpha$ -phenylselenoketones to allylic selenides by way of the phenylseleno migration This method provides a one carbon homologative preparation of various primary allylic selenides starting from  $\alpha$ -phenylselenoketones, which are easily available from ketones.

## Refereces and Notes

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- 2. P.F. Hudrlik and D. Peterson, J. Am. Chem. Soc., <u>97</u>, 1464 (1975) and references therein.
- 3. <sup>1</sup>H NMR (60 MHz, CDCl<sub>3</sub>, TMS) <u>5</u>, § 4.57 (s, C=CH<sub>2</sub>), <u>6</u>, § 3 50 (s, SeCH<sub>2</sub>)ppm.
- 4. Krief demonstrated an alternative transforamtion of 2-hydroxy-1-trimethyl-silylethyl selenide to vinylic selenide and vinylsilane via syn (basic condn.) and anti (acidic condn.) elimination, respectively See
  W. Dumont, V. Ende, and A Krief, Tetrahedron Lett, 1979, 485.
- 5. Brownbridge reported that acid-catalyzed rearrangement of 2-hydroxyalkyl sulfide lead to phenylthic migration even from a secondary to a tertiary center, when assisted by trimethylsilyl group. See P Brownbridge, I. Fleming, A. Pearce, and S Warren, J. Chem Soc., Chem. Comm., <u>1976</u>, 751.

(Received in Japan 28 June 1982)