

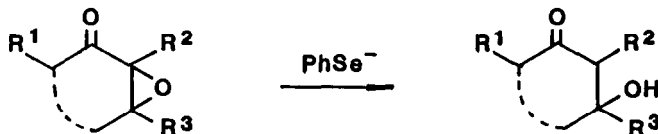
**SODIUM PHENYLSELENO(TRIETHOXY)BORATE, Na<sup>+</sup>[PhSeB(OEt)<sub>3</sub>]<sup>-</sup>: THE REACTIVE SPECIES GENERATED FROM (PhSe)<sub>2</sub> WITH NaBH<sub>4</sub> IN ETHANOL**

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**Summary:** The reactive species generated from (PhSe)<sub>2</sub> with NaBH<sub>4</sub> in ethanol has been demonstrated to be a sodium phenylseleno(triethoxy)borate complex, Na<sup>+</sup>[PhSeB(OEt)<sub>3</sub>]<sup>-</sup>, as evidenced in the reduction of α,β-epoxy ketones leading to β-hydroxy ketones.

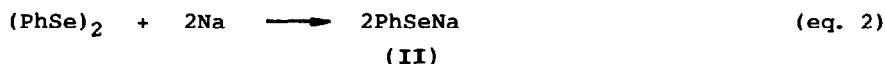
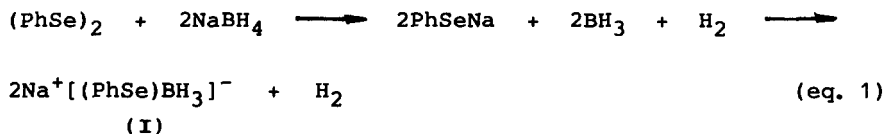
The utility of areneselenide anions for effecting a wide variety of synthetic transformations is now well-established.<sup>1</sup> Among them, sodium benzene selenolate (PhSeNa) has been widely used as the most common reagent<sup>1</sup> since it can be readily prepared by reduction of diphenyl diselenide ((PhSe)<sub>2</sub>) with sodium borohydride (NaBH<sub>4</sub>) in ethanol (method A),<sup>2</sup> or with Na metal in dry THF (method B).<sup>3</sup>

We have recently reported that "phenyl selenide anion" generated by the method A serves as an efficient reagent for the reduction of α,β-epoxy ketones to β-hydroxy ketones and by this method a wide variety of cyclic and acyclic aldols are readily accessible.<sup>4</sup> In this letter we document that "phenyl

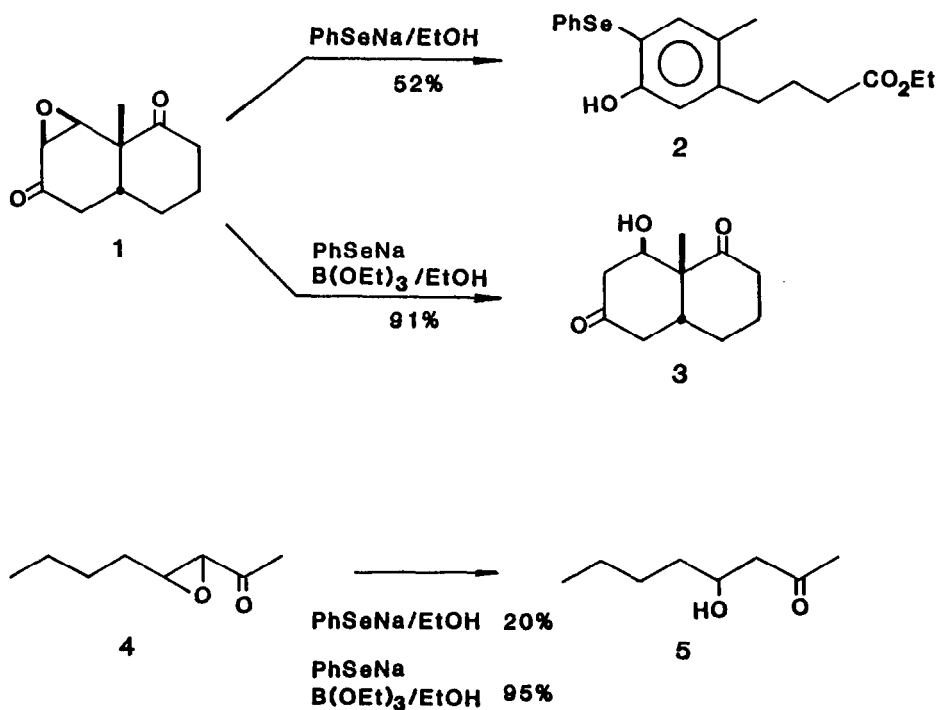


selenide anion" generated by the method A, NaBH<sub>4</sub> reduction of (PhSe)<sub>2</sub>, is actually a sodium phenylseleno(triethoxy)borate complex, Na<sup>+</sup>[PhSeB(OEt)<sub>3</sub>]<sup>-</sup>, which plays a crucial role in the reduction of epoxy ketones.

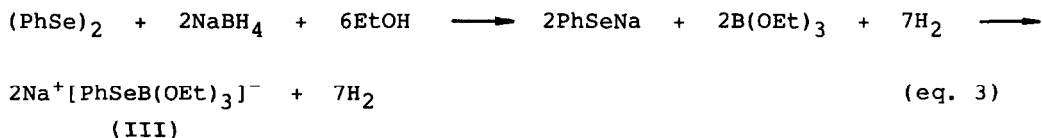
It has been proposed by Liotta that "phenyl selenide anion" generated by the method A is a sodium phenylseleno(trihydro)borate complex Na<sup>+</sup>[(PhSe)BH<sub>3</sub>]<sup>-</sup> (I) (eq. 1) in contrast with uncomplexed PhSeNa (II) generated by the method B (eq. 2).<sup>3</sup>



We investigated the behavior of both selenide anions in the reduction of epoxy ketones to clarify the reactive species as well as the reaction mechanism. As a result, the following remarkable discrepancy was observed. Thus the reaction of epoxy ketone **1**<sup>5</sup> with 3 equiv. of uncomplexed PhSeNa, prepared by the method B,<sup>3</sup> in ethanol<sup>6</sup> containing 0.5 equiv. of AcOH<sup>7</sup> yielded an unexpected aromatic compound **2** as the major product (52%),<sup>8</sup> and the reduction product **3** was not formed at all. This result was rather surprising because treatment of **1** with 3 equiv. of "phenyl selenide anion", generated by the method A, in ethanol containing 0.5 equiv. of AcOH<sup>7</sup> resulted in the formation of the single product **3** (95%) as recently reported.<sup>4</sup> We assumed that this difference may be due to the intermediacy of triethyl borate (B(OEt)<sub>3</sub>) generated in situ (vide post). Indeed, addition of B(OEt)<sub>3</sub> (3 equiv.) in the former reaction resulted in the formation of **3** (91%) as the sole product instead of **2**. Similarly, on treatment with the combination of uncomplexed PhSeNa and B(OEt)<sub>3</sub> in ethanol, acyclic epoxy ketone **4** produced the reduction product **5** in 95% yield, whereas use of uncomplexed PhSeNa alone resulted in a lower yield of the product (20%).<sup>9</sup>



These outcomes imply that "phenyl selenide anion" generated by the method A is a sodium phenylseleno(triethoxy)borate complex,  $\text{Na}^+[\text{PhSeB}(\text{OEt})_3]^-$  (III) (eq. 3), and not the phenylseleno(trihydro)borate complex,  $\text{Na}^+[(\text{PhSe})\text{BH}_3]^-$  (I) (eq. 1) as previously proposed.<sup>3</sup>



This assumption was further confirmed by the following stoichiometric experiments. According to the equations (1) and (3), the quantity of hydrogen evolution is different, i.e., 1 mole and 7 moles, respectively. Actually, 7.5 molar equiv. of  $\text{H}_2$  was evolved in the experiment using the method A, which is consistent with the stoichiometry of eq. 3.<sup>10</sup> Furthermore, we examined whether "phenyl selenide anion" prepared by the method A actually forms the complex III or not. As anticipated, the complex III was readily isolated as white solid by the evaporation of solvent (ethanol) in vacuo and its weight was consistent with the stoichiometry of the formula 3.<sup>11</sup> In addition, the NMR spectrum ( $\text{CDCl}_3$ ) of this solid revealed two signals due to ethoxy protons at  $\delta$ 1.24 ppm (br t,  $J=7$  Hz) and 3.70 ppm (br s,  $W_{1/2}=24$  Hz) besides aromatic protons. These results unequivocally establish the formation of the complex III according to eq. 3.

In conclusion, we have presented clear evidence that the reactive species generated by reduction of  $(\text{PhSe})_2$  with  $\text{NaBH}_4$  in ethanol (method A) is a sodium phenylseleno(triethoxy)borate complex III, which played a crucial role in the reduction of  $\alpha, \beta$ -epoxy ketones to  $\beta$ -hydroxy ketones.<sup>12</sup>

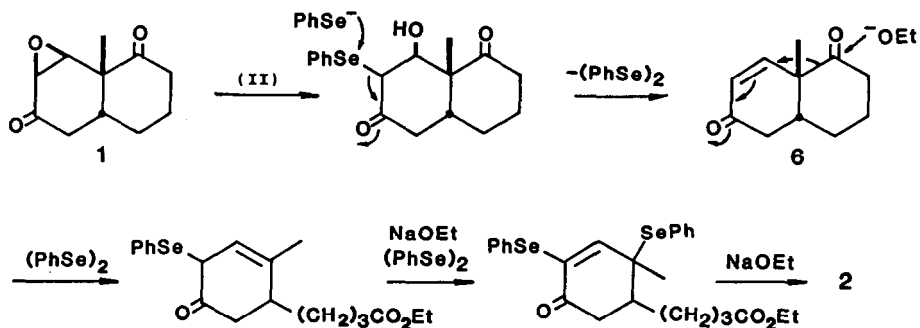
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#### References and Notes

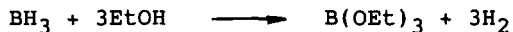
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6. Uncomplexed PhSeNa was prepared in THF according to the method of Liotta<sup>3</sup> and the solvent was replaced by ethanol.
7. AcOH was added as a scavenger for alkoxides which might be generated on the

preparation of benzeneselenolate (cf. ref. 4).

8. The product 2 was probably derived from ene-dione 6 since the latter afforded the same compound 2 in a similar yield (52%) on treatment with NaOEt and  $(\text{PhSe})_2$  in ethanol.



9. A lower yield was probably due to the generation of sodium ethoxide in the reaction media which would cause many side reactions such as dehydration, the retrograde aldol reaction, Michael reaction, etc. since many other by-products were formed.
10. The result clearly demonstrates that  $\text{BH}_3$  generated in situ (eq. 2) was immediately transformed into  $\text{B}(\text{OEt})_3$  by the solvent according to the following equation. We also ascertained this stoichiometry by addition of a THF solution of borane (Aldrich, 1 M/dm<sup>-3</sup> solution) to ethanol followed by measurement of hydrogen evolution.



11. Provided the complex III was not formed,  $\text{B}(\text{OEt})_3$  (bp 117 °C) should be readily removed in vacuo.
12. Study of the detailed reaction mechanism including the role of triethyl borate is in progress.

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