## Synthesis of 1,1'-Binaphthyl-2,2'-diyl Phosphoroselenoic Ammonium Salts and Their Conversion to Optically Active Dialkyl Diselenides

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Optically pure phosphoroselenoyl chloride reacted with  $Et_3N$  in the presence of  $H_2O$  to give a phosphoroselenoic tertiary ammonium salt. Formation of the salt was confirmed by X-ray molecular structure analysis. The quaternary ammonium salt was prepared by reacting phosphoroselenoic acid *O*-2-silylethyl ester with  $Bu_4NF$ . The alkylation of tertiary ammonium salt with racemic alkyl halides gave phosphoroselenoic acid *Se*-esters as diastereomeric mixtures. The cleavage of *Se*-esters with  $Bu_4NF$  gave optically active dialkyl diselenides.

Intensive studies on optically active phosphoric acids bearing a 1,1'-binaphthyl-2,2'-diyl group have recently been performed, and particularly on their use as organocatalysts.<sup>1</sup> Sulfur isologues of phosphoric acids have also been prepared by reacting 1,1'-binaphthyl-2,2'-diol with thiophosphoryl chloride<sup>2</sup> or phosphorus pentasulfide.<sup>3</sup> The acids obtained are used to prepare optically active organosulfur compounds.<sup>2,4</sup> In contrast, no examples of the selenium isologues of phosphoric acids and salts have been reported, although several types of phosphoroselenoic acid salts bearing alkyl or phenyl groups on the oxygen atom have been prepared, and their reactivity has been elucidated.<sup>5</sup>

During the course of our studies on the compounds bearing P=Se bonds,<sup>6</sup> we recently found that phosphoroselenoyl chloride **1** could be used as a new molecular tool to discriminate racemic alcohols and to obtain optically active alcohols, amines, and phosphoramidites.<sup>7</sup> We report here the synthesis of optically pure phosphoroselenoic acid salts from **1** and their reactions with racemic alkyl halides. A new method for preparing optically active dialkyl diselenides is also described.



Scheme 1.

The reaction of chloride **1** with  $Et_3N$  (3 equiv.) and  $H_2O$  (2 equiv.) went to completion within 2 h under reflux in THF to give tertiary salt **2** in 98% yield as a white solid (Scheme 1).<sup>8</sup> Formation of the salt **2** was confirmed by X-ray structure analysis.<sup>9</sup> The salt **2** was highly soluble in  $CH_2Cl_2$ , but less soluble in THF and toluene.

Alternatively, the quarternary ammonium salt **4** was synthesized by reacting phosphoroselenoic *O*-2-(trimethylsilyl)ethyl ester  $3a^8$  with Bu<sub>4</sub>NF. Elimination of a silyl group and ethylene from 3a proceeded smoothly to give the corresponding salt **4** in 75% yield (Scheme 2).

During the synthesis of **3a**, Se-ester **3b**<sup>8</sup> was also formed



## Scheme 2.

as a byproduct. Initially, a similar reaction of **3b** and Bu<sub>4</sub>NF leading to **4** was expected. However, in the latter case, diselenide **5** was exclusively obtained along with 1,1'-binaphthyl-2,2'-diol. The selective cleavage of P–Se and P–O bonds takes place rather than desilylation. To the best of our knowledge, this is the first example of fluoride anion-mediated hydrolysis of phosphoroselenoic acid *Se*-esters, although precedents regarding the substitution reaction of esters with fluoride ions have been reported.<sup>10</sup> These critical differences in the reaction course may be due to the subtle differences in the dissociation energies of these bonds (P–O: 599.1 ± 12.6 kJ/mol, P–Se:  $363 \pm 10.0 \text{ kJ/mol}$ , P–F:  $439 \pm 96 \text{ kJ/mol}$ , Si–F:  $552.7 \pm 2.1 \text{ kJ/mol}$ ).<sup>11</sup>

The signals due to the phosphorus atoms in 2 and 4 were observed at  $\delta$  62.1 and 58.4, respectively, in <sup>31</sup>P NMR spectra, whereas <sup>77</sup>Se NMR spectra showed signals at  $\delta$  –234.95 and –217.9. The coupling constants between the phosphorus and selenium atoms in 2 and 4 were 878.4 and 854.0 Hz; i.e. larger than the value of the *Se*-ester **3b** (572.4 Hz), and smaller than that of *O*-ester **3a** (1012.5 Hz). These results suggest that the phosphorus–selenium bonds in salts 2 and 4 possess double-bond character to some extent.

Alkylation of the salt 2 was carried out and the results are shown in Table 1. In all cases, alkylation took place at the selenium atom of the salt 2. The formation of Se-esters 7 was confirmed by <sup>31</sup>P and <sup>77</sup>SeNMR spectra and by the coupling constants between phosphorus and selenium atoms. The 2-butenylation of 2 with 6a was complete within 4 h at rt (Entry 1), whereas the reaction of 2 with cyclohexenyl bromide (6b) required reflux temperature in CH<sub>2</sub>Cl<sub>2</sub>. Similarly, the reaction of 2 with 1-phenethyl bromide (6c), 2-naphthylethyl bromide (6d), 2-bromobutane (6e), and  $\alpha$ -bromopropionic acid ester 6f was carried out under reflux in CH<sub>2</sub>Cl<sub>2</sub> or toluene. The reaction of racemic alkyl halides 6b-6f gave the diastereomeric mixtures of 7b-7f in almost equal ratios. These diastereomers were discriminated by <sup>31</sup>P and <sup>77</sup>Se NMR spectra. Some of the diastereomers were separated by the fractional recrystallization. For 7c, diastereomers were separated by HPLC.

Finally, the cleavage of phosphoroselenoic acid *Se*-esters 7 was carried out with  $Bu_4NF$ , as found in Scheme 2. Diastereomerically pure ester 7c was treated with  $Bu_4NF$  (1.5 equiv.) in

**Table 1.** Reaction of phosphoroselenoic acid salt  $\mathbf{2}$  with alkyl halides<sup>a</sup>



<sup>a</sup>The salt **2** was reacted with alkyl halide 6 (1–5 equiv.) in an apporpriate solvent unless otherwise noted. <sup>b</sup>Isolated yield. <sup>c</sup>THF was used as a solvent. <sup>d</sup>CH<sub>2</sub>Cl<sub>2</sub> was used as a solvent. <sup>e</sup>Toluene was used as a solvent.

$$\begin{array}{c} O \\ O \\ P^{-}Se \\ \hline P \\ Se \\ \hline P \\ Se \\ \hline P \\ Se \\ \hline P \\ Se \\ Se \\ \hline P \\ \hline P \\ Se \\ Se \\ \hline P \\ \hline Se \\ \hline P \\ \hline Se \\ Se \\ \hline P \\ \hline P \\ \hline Se \\ \hline Se \\ \hline P \\ \hline Se \\ \hline Se \\ \hline P \\ \hline Se \\ \hline Se$$

1

## Scheme 3.

THF for 1.5 h to give optically active diselenide **8** in 81% yield,<sup>12</sup> although the absolute configuration of **8** has not yet been determined (Scheme 3).

In summary, we have demonstrated the synthesis and alkylation of the phosphoroselenoic acid salt bearing a 1,1'-binaphthyl-2,2'-diyl group. The separation and cleavage of the resulting esters have provided a new route to optically active dialkyl diselenides, which are not readily accessible by known methods.<sup>13</sup>

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