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## Synthesis of novel organoselenium as catalyst for Baeyer–Villiger oxidation with 30% H<sub>2</sub>O<sub>2</sub>

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Abstract—A novel diselenide was synthesized in good yield via only four steps from phenol, and was employed as the catalyst for the Baeyer–Villiger oxidation with  $30\% H_2O_2$  to obtain lactones in good yields. © 2005 Elsevier Ltd. All rights reserved.

The Baeyer–Villiger oxidation, which uses organic peroxy acids as oxidants, has been commonly employed for the preparation of esters.<sup>1</sup> In particular, the ease of transformation from cyclic ketones to lactones makes it an important method for the total syntheses of natural products.<sup>2</sup> However, such peroxy acids as trifluoroperacetic acid and *m*-chloroperbenzoic acid, which are the most popular oxidants for the Baeyer–Villiger oxidation, are explosive and therefore should be handled with extreme care. Moreover, the storage of large amounts of such peroxy acids is not desirable, and the generation of much waste acid after the oxidation has hindered its use in the industry. To overcome these problems, hydrogen peroxide has been employed as an alternative.<sup>3</sup> On the other hand, several selenium compounds are efficient reagents for the oxidation of organic compounds.<sup>4</sup> For example, the oxidation of olefin compounds with a selenium dioxide takes place selectively at the allylic position. Recently, Sheldon and co-workers reported that organoselenium compounds bearing trifluoromethyl groups could catalyze the oxidation of olefins and cyclic ketones with 60% hydrogen peroxide in fluorous solvent to obtain epoxides and lactones, respectively.<sup>4d-f</sup> The diselenides are reacted with excess hydrogen peroxide to obtain peroxyseleninic acids that serve as catalysts for the Baeyer–Villiger oxidation. In this paper, we describe the synthesis of novel organic selenium compounds that catalyze the Baeyer–Villiger



Figure 1. Catalytic cycle of seleninic acids with H2O2 in Baeyer-Villiger oxidation.

Keywords: Baeyer-Villiger oxidation; Diselenide; Seleninic acid; Hydrogen peroxide.

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Table 1. The diselenides catalyzed Baeyer–Villiger oxidation with 30%  $\rm H_{2}O_{2}$ 

<sup>a</sup> Isolated yield.

<sup>b</sup> The starting material was recovered in 75%.

oxidation with 30% hydrogen peroxide in dichloromethane (Fig. 1).

Novel organoselenium catalysts were synthesized in only four steps from phenol in good yields. After phenol was protected by MOM ether, *ortho*-lithiation of the ether with *n*-BuLi generated lithium salt as a white suspension. The addition of selenium powder, followed by bubbling air, produced diselenide 1. Without purification of 1, deprotection of the MOM ether proceeded with 1 M HCl in methanol with heating to reflux. Bisphenol 2 was deprotonated by reacting with *N*-ethyldiisopropylamine, followed by reacting with trifluoromethanesulfonic anhydride at -40 °C in dichloromethane under nitrogen to obtain diselenide bearing bistriflate **3** (Scheme 1).<sup>5</sup>

Novel diselenide **3** and other diselenides were used as the catalyst for the Baeyer–Villiger oxidation of 4-phenylcyclohexanone with 30% hydrogen peroxide (Table 1). As a result, only diselenide **3** catalyzed the oxidation to obtain the corresponding lactone in 85% yield, whereas the other diselenides did not promote any oxidation.<sup>6</sup> In addition, when the trifluoromethanesulfonic acid (TfOH) was added as an additive to the oxidation of 4-phenylcyclohexanone with catalyst **2** and hydrogen peroxide, the starting material was almost recovered (entry 6). Thus, it seems that the diselenide **3** bearing the trifluoromethanesulfonate (TfO) group at *o*-position is very important for catalyst.

This oxidation catalyzed by diselenide proceeded via seleninic acid. Thus, the oxidation of ketone was carried out with seleninic acid as the catalyst under the same conditions as those used for the case of diselenide. Seleninic acid was isolated from the diselenide and 30% hydrogen peroxide. When the oxidation of 4-phenyl-cyclohexanone was carried out with seleninic acid as the catalyst, the corresponding lactone was obtained in a similar yield (Scheme 2).

The Baeyer–Villiger oxidation catalyzed by diselenide **3** with 30% hydrogen peroxide was applied to various ketones (Table 2). The oxidation of 4-phenylcyclohexanone proceeded in 77% and 84% yields for 8 and 16 h, respectively (entries 1 and 2). Reducing the amount of catalyst led to a lower product yield (entry 4). Other cyclic ketones were also transformed into the corresponding lactones in good yields.

The oxidation of aromatic aldehyde is also catalyzed by deselenide.<sup>4b</sup> 2,5-Dimethoxybenzaldehyde was reacted with 30% hydrogen peroxide and 0.05 equiv of **3** to produce 2,5-dimethoxyphenol in 99% yields (Scheme 3). The time to accomplish the oxidation of the aldehyde was only 3 h when catalyst **3** was used, though the







$($ $)$ $)$ $)_2$ , 5 equiv 30% H <sub>2</sub> O <sub>2</sub>				
R <sup>⊥</sup> R'		⊂ CH <sub>2</sub> Cl <sub>2</sub> , rt		
Entry	Ketone	Catalyst (mol %)	Time (h)	Yield (%)
1 2 3 4	O Ph	5 5 5 0.5	8 16 24 22	77 84 85 32
5		5	17	90
6		5	17	99
7		5	22	41
8	>	5	65	59

Table 2. Baeyer–Villiger oxidation with 30% H<sub>2</sub>O<sub>2</sub> for various ketones



Scheme 3.

diphenyl diselenide needed to oxidize the aldehyde for 20 h. $^{4b}$ 

The typical procedure is as follows: Diselenide **3** dissolved in dichloromethane was added dropwise to 30% hydrogen peroxide at rt. After stirring for 0.5 h, ketones were added to the reaction mixture. The resulting mixture was poured into saturated NH<sub>4</sub>Cl solution and extracted with dichloromethane. The organic layer

was washed with brine and dried over MgSO<sub>4</sub>. After filtration and evaporation of the solvent, the residue was purified by column chromatography on silica gel.

In conclusion, the synthesis of novel diselenide was achieved in good yield via only four steps from phenol. It was clarified that diselenide **3** is an excellent catalyst for the Baeyer–Villiger oxidation without fluorous solvent. Further studies of the epoxidation and regio-selectivity of the oxidation with **3**, and the synthesis of asymmetric and reusable organoselenium catalysts are ongoing.

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 Bis(2-phenyltrifluoromethanesulfonate)diselenide 3; pale yellow powder; mp 55 °C; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ 7.25–7.43 (m, 3H), 7.76–7.80 (m, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 148.8, 135.7, 130.0, 128.8, 123.5, 121.6, 118.3 (q, 
$$\begin{split} J_{\rm C-F} &= 316.3 \text{ Hz}); \ ^{77} \text{Se NMR (95 MHz, CDCl_3): } \delta \ 420.7; \text{ IR} \\ \nu \ 3090, \ 2350, \ 1917, \ 1790, \ 1563, \ 1457, \ 1040 \ \text{cm}^{-1}; \ \text{HRMS} \\ \text{calcd for } (\text{M}^+) \ \text{C}_{14} \text{H}_8 \text{F}_6 \text{O}_6 \text{S}_2 \text{Se}_2 \ 609.7997, \ found \ 609.8001. \end{split}$$

6. The oxidation of 4-phenylcyclohexanone with 12 equiv of 30% hydrogen peroxide and 0.5 equiv of diphenyl diselenide as a catalyst for 24 h gave a mixture of the corresponding lactone (10%), the hydrolysis product of the lactone (22%), the  $\alpha$ , $\beta$ -unsaturated ketone (trace) and the recovered cyclohexanone (50%). When the catalytic amount of **3** was used in the oxidation, the corresponding lactone was only prepared and no side products were obtained.