

PREPARATION OF  $\alpha$ -TRIALKYLSILYL KETONES FROM  $\alpha$ -PHENYLSELENO DERIVATIVES VIA  
THEIR SILYL ENOL ETHERS

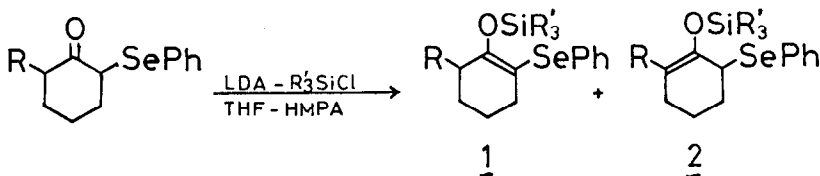
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Summary: On treatment with metallic lithium in the presence of dimethylamino-naphthalene, trialkylsilyl enol ethers of  $\alpha$ -phenylseleno ketones were converted into the corresponding  $\alpha$ -trialkylsilyl ketones in good yields.

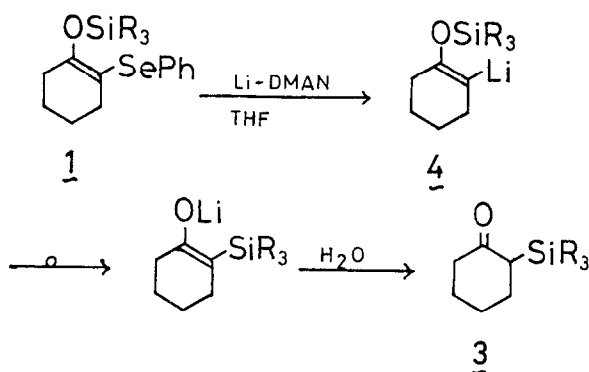
Silyl enol ethers have widely been employed as versatile synthetic materials and various synthetic methods have been devised for their regio-controlled preparation.<sup>1)</sup> Recently, unique reactivities of their structural isomers,  $\alpha$ -trialkylsilyl ketones, have also been recognized,<sup>2)</sup> but their preparative methods are now quite limited.<sup>3)</sup> Especially, difficulties are usually encountered in the preparation of cyclic ketone derivatives possessing sterically hindered silyl groups.

We have been interested in the generation of reactive species utilizing a facile cleavage of weak carbon-selenium bonds under the influence of alkyl-lithiums or alkali metal.<sup>4)</sup> Examination of this procedure with silyl enol ethers of  $\alpha$ -phenylseleno carbonyl compounds led us to finding a general method for the preparation of such compounds having various trialkylsilyl groups.

Recent development of organoselenium chemistry has offered several useful methods for regioselective synthesis of  $\alpha$ -phenylseleno carbonyl compounds.<sup>5)</sup> Various  $\alpha$ -phenylseleno ketones could be converted into the corresponding silyl enol ethers in highly regio-controlled manner. For example, 2-phenylseleno-6-methylcyclohexanone gave the silyl enol ether 1 (R = CH<sub>3</sub>) in 87% yield when treated with lithium diisopropylamide (LDA) and t-butyltrimethylsilyl chloride in THF-HMPA at -78°C. Similarly, silylation of 2-phenylseleno-cyclohexanone at 0°C afforded the corresponding ether 1 (R = H) in 82% yield along with a trace amount of the regio-isomer 2 (R = H).<sup>6)</sup>



In order to cleave the carbon-selenium bond, the silyl enol ether 1 (R = H) was treated with metallic lithium (6 eq) and dimethylaminonaphthalene (DMAN) (0.2 eq)<sup>7)</sup> in THF at -50°C. After 1 hr when the starting material 1 was completely disappeared, it was quenched with water. Product analyses of the reaction mixture showed that 2-t-butyltrimethylsilylcyclohexanone 3 was formed in 70% yield along with the deselenylated product, 1-t-butyltrimethylsilyloxycyclohexene (15%). When a similar reaction was carried out at 0°C, 3 (85%) was obtained exclusively. In both cases, the selenium moiety was recovered in ca. 90% yield as diphenyl diselenide by column chromatography. From these results, bond cleavage appears to take place preferentially between vinyl carbon and selenium to yield the corresponding trialkylsilyloxyvinyl lithium intermediate 4, which undergoes a facile rearrangement of silyl group from oxygen to the anionic carbon site to give the enolate of 2-t-butyltrimethylsilylcyclohexanone 3.



As shown in the Table, various silyl enol ethers of  $\alpha$ -selenylated cyclic ketones could be converted into the corresponding  $\alpha$ -trialkylsilyl ketones<sup>8)</sup> in good yields by the present procedure. Except diphenyl diselenide, formation of any other by-products was not detected.

In contrast to the cyclic ketone derivatives, the reaction of silyl enol ethers of acyclic ketones accompanied formation of the corresponding acetylenic compounds as by-products, which may result from  $\beta$ -elimination of siloxyvinyl-

lithium intermediates. For example, the reaction of dimethylisopropylsilyl enol ether of  $\alpha$ -phenylselenobutyrophenone afforded  $\alpha$ -dimethylisopropylsilylbutyrophenone (67%) and 1-phenyl-1-butyne (17%). Further, with a phenylselenomethylketone derivative, terminal acetylene formed through this process may also act as a proton source to decompose the siloxyvinyl lithium intermediate, which sometimes leads to the formation of deselenylated silyl enol ether as shown in the Table.

Table. Preparation of  $\alpha$ -Trialkylsilyl Ketones 3.



R <sup>1</sup>	R <sup>2</sup>	SiR' <sub>3</sub>	Product (Yield)
-(CH <sub>2</sub> ) <sub>3</sub> -		t-BuSiMe <sub>2</sub>	<u>3</u> (79%)
-(CH <sub>2</sub> ) <sub>4</sub> -		SiEt <sub>3</sub>	<u>3</u> (75%)
-(CH <sub>2</sub> ) <sub>4</sub> -		i-PrSiMe <sub>2</sub>	<u>3</u> (82%)
-(CH <sub>2</sub> ) <sub>4</sub> -		t-BuSiMe <sub>2</sub>	<u>3</u> (85%)
$\begin{array}{c} \text{CH}_3 \\   \\ -\text{CH}(\text{CH}_2)_3- \\   \\ \text{C}_4\text{H}_9 \end{array}$		t-BuSiMe <sub>2</sub>	<u>3</u> (84%)
-CH(CH <sub>2</sub> ) <sub>3</sub> -		i-PrSiMe <sub>2</sub>	<u>3</u> (81%)
-(CH <sub>2</sub> ) <sub>6</sub> -		i-PrSiMe <sub>2</sub>	<u>3</u> (83%)
-(CH <sub>2</sub> ) <sub>10</sub> -		t-BuSiMe <sub>2</sub>	<u>3</u> (78%)
C <sub>6</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	i-PrSiMe <sub>2</sub>	<u>3</u> (67%), C <sub>6</sub> H <sub>5</sub> C≡CC <sub>2</sub> H <sub>5</sub> (17%)
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub>	H	t-BuSiMe <sub>2</sub>	<u>3</u> (57%), C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub> C≡CH (14%), C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub> C(OSiMe <sub>2</sub> -t-Bu)=CH <sub>2</sub> (15%)
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub>	C <sub>3</sub> H <sub>7</sub>	i-PrSiMe <sub>2</sub>	<u>3</u> (65%), C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub> C≡CC <sub>3</sub> H <sub>7</sub> (17%)

References and Notes

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