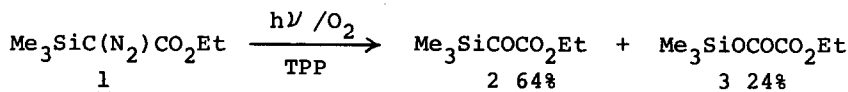
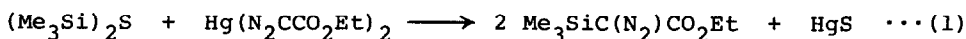


SYNTHESIS OF SILYL KETONE BY THE PHOTSENSITIZED  
OXYGENATION OF SILYL DIAZO COMPOUNDS

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Silyl ketones are of special interest in their chemical properties and also their unique spectral behavior in the ultraviolet and infrared spectra as well. They must be prepared under relatively mild and neutral conditions to avoid silicon-carbonyl carbon bond cleavage. Successful synthetic routes of silyl ketones have been reported by Brook<sup>1)</sup> and the other groups.<sup>2)</sup> Although these methods have been employed for the synthesis of silyl ketones, there is no synthetic method of silyl ketones possessing a functional group such as carbonyl. We have found entirely new method for the synthesis of silyl ketones with ester group in the photosensitized oxygenation of silyl diazo esters.<sup>3)</sup>



In a typical reaction, a mixture of 1.0 mmol of silyl diazoacetate 1 and 10 ml of carbon tetrachloride containing ca. 30 mg of TPP (meso-Tetraphenylporphine) as sensitizer was photolyzed in a water cooled Pyrex tube with 300W halogen lamp under bubbling oxygen for 1.9 hr. Analysis of the reaction mixture by GLC showed two products and unreacted 1 (5%). The yields of products were determined by GLC on addition of internal standard to the reaction mixture. The products were collected by preparative GLC and found to be silyl ketone 2 and silyl oxalate 3 by their spectroscopic data. The latter was prepared independently from the reaction of diethyl oxalate and trimethylsilyl iodide by the method of Jung.<sup>4)</sup> We isolated the silyl ketone 2 in 40% yield by the preparative GLC from the reaction mixture, but separation on silica gel chromatography did not give satisfactory results due to presumably decomposition of 2. Silyl ketones having ester group, 4 and 5, were also prepared in moderate yields by a similar method from the corresponding silyl diazo esters. The results and their spectroscopic data of the new silyl ketones are given in Table I and II.

Aryl silyl ketones, 6, 7, and 8, were also obtained in the photosensitized oxygenation of aryl silyl diazomethanes.<sup>5)</sup>

Table I. Photosensitized Oxygenation of Silyl Diazo Compounds.<sup>a</sup>

Silyl Diazo Compd.	Reaction Time(hr)	Silyl Ketone	Yield(%) <sup>b</sup>	
Me <sub>3</sub> SiC(N <sub>2</sub> )CO <sub>2</sub> Et	2.0 mmol	5	<u>2</u> Me <sub>3</sub> SiCOCO <sub>2</sub> Et	40
Me <sub>3</sub> SiC(N <sub>2</sub> )CO <sub>2</sub> Me	2.0 mmol	12	<u>4</u> Me <sub>3</sub> SiCOCO <sub>2</sub> Me	42
PhMe <sub>2</sub> SiC(N <sub>2</sub> )CO <sub>2</sub> Me	2.0 mmol	12	<u>5</u> PhMe <sub>2</sub> SiCOCO <sub>2</sub> Me	43
Me <sub>3</sub> SiC(N <sub>2</sub> )Ph	4.0 mmol	0.5	<u>6</u> Me <sub>3</sub> SiCOPh <sup>c</sup>	42 <sup>d</sup>
PhMe <sub>2</sub> SiC(N <sub>2</sub> )Ph	0.7 mmol	0.2	<u>7</u> PhMe <sub>2</sub> SiCOPh	(51) <sup>e</sup>
Ph <sub>3</sub> SiC(N <sub>2</sub> )Ph	2.0 mmol	0.7	<u>8</u> Ph <sub>3</sub> SiCOPh <sup>c</sup>	64

- a. The reaction was carried out in carbon tetrachloride using TPP as sensitizer. All silyl ketones in Table I are yellow.
- b. Isolated yields are given. Parenthesis shows GLC yield.
- c. Silyl ketones, 6 and 8, were separated on silica gel chromatography.  
7: mp 53-54°C (lit. mp 54-55°C<sup>1</sup>); 8: mp 103-104°C (lit. mp 102-103°C<sup>1</sup>).
- d. Trimethylsilyl benzoate was also obtained.
- e. Dimethylphenylsilyl benzoate was also obtained.

Table II. Spectroscopic Data of Silyl Ketone, 2, 4, and 5.

<u>2</u> :	NMR(CCl <sub>4</sub> ) δ 0.33(s, 9H, SiMe), 1.40(t, 3H, J=7Hz, CCH <sub>3</sub> ), 4.27(q, 2H, J=7Hz, OCH <sub>2</sub> ); IR(NaCl) 1740 and 1710(CO <sub>2</sub> Et), 1660cm <sup>-1</sup> (SiCO); UV(C <sub>6</sub> H <sub>12</sub> ) λ <sub>max</sub> (ε) 455(97), 230(388).
<u>4</u> :	NMR(CCl <sub>4</sub> ) δ 0.28(s, 9H, SiMe), 3.70(s, 3H, CO <sub>2</sub> Me); IR(NaCl) 1740 and 1710(CO <sub>2</sub> Me), 1660cm <sup>-1</sup> (SiCO); UV(C <sub>6</sub> H <sub>12</sub> ) λ <sub>max</sub> (ε) 455(100), 227(254).
<u>5</u> :	NMR(CCl <sub>4</sub> ) δ 0.53(s, 6H, SiMe), 3.63(s, 3H, CO <sub>2</sub> Me), 7.1-7.6(m, 5H, ArH); IR(NaCl) 1750 and 1720(CO <sub>2</sub> Me), 1660cm <sup>-1</sup> (SiCO); UV(C <sub>6</sub> H <sub>12</sub> ) λ <sub>max</sub> (ε) 455(213), 279(620).

## References and Notes

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- 5) Aryl silyl diazomethanes, Me<sub>3</sub>SiC(N<sub>2</sub>)Ph, PhMe<sub>2</sub>SiC(N<sub>2</sub>)Ph, Ph<sub>3</sub>SiC(N<sub>2</sub>)Ph, were prepared from the corresponding silyl ketones, 6, 7, and 8; K.D.Kaufmann, B.Aurath, P.Träger, and K.Rühlmann, *Tetrahedron Lett.*, 4973 (1968).