

science temperature was not obtained successfully because of thermal decomposition of **1** at above 100°C.

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- Data: HRMS (70 eV EI, m/z) calcd. for C<sub>16</sub>H<sub>32</sub>FeN<sub>3</sub>O<sub>7</sub>PSi: 493.1088. Found: 493.1079. <sup>1</sup>H-NMR (δ): 1.32, 1.37 (dd, <sup>3</sup>J = 6.0 Hz, Me<sub>2</sub>CH, 6H), 2.20 (d, <sup>3</sup>J<sub>PH</sub> = 10.4 Hz, Me<sub>2</sub>N, 9H), 4.85(h, <sup>3</sup>J = 6.0 Hz, Me<sub>2</sub>CH, 2H). <sup>13</sup>C[<sup>1</sup>H]NMR (δ): 25.73 (s, Me<sub>2</sub>CH), 25.74 (s, Me<sub>2</sub>CH), 36.43 (d, <sup>3</sup>J<sub>PC</sub> = 6.0 Hz, Me<sub>2</sub>N), 65.00 (s, Me<sub>2</sub>CH), 218.07 (s, CO<sub>eq</sub>), 221.02 (s, CO<sub>ap</sub>). <sup>29</sup>Si[<sup>1</sup>H]NMR (δ): 20.9 (d, <sup>2</sup>J<sub>PSi</sub> = 25.6 Hz). IR (cm<sup>-1</sup>): 2007, 1926, 1888 (ν<sub>CO</sub>, THF soln), 765 (ν<sub>PN</sub>, KBr pellet).

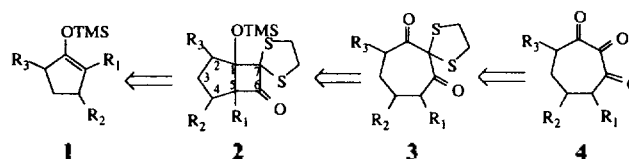
## Ring Cleavage of Cycloadduct from [2+2] Thermal Cycloaddition of Dimethylene Dithioketene to Silyl Enol Ether

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Cycloadducts derive from [2+2] photoaddition<sup>1</sup> or thermal addition<sup>2</sup> have been utilized for the construction of various natural product skeletons.<sup>3</sup> Fragmentation of the cycloadducts was usually performed by ionic and thermal reactions.<sup>4</sup> Radical type fragmentation was also reported.<sup>5</sup> Recently, we reported a ring expansion methodology to prepare



Scheme 1.

Table 1. Cycloaddition and Fragmentation Products from Silyl Enol Ether

Entry	Silyl enol ethers	Cycloadducts <sup>a,b</sup> (yield %)	Fragmentation products <sup>c,d</sup>
1			
2			
3			
4			
5		No Reaction	
6			
7		No Reaction	
8			

<sup>a</sup>Isolated yields after column chromatography. <sup>b</sup>Yields based on 2-chloro carbonyl thiolane. <sup>c</sup>Diketone is in equilibrium with enol forms (by <sup>1</sup>H-NMR). <sup>d</sup>Isolated yields without further purification are quantitative. (one spot on TLC).

substituted cycloheptenones *via* fragmentation of the corresponding 1-trimethylsilyloxy bicyclo [3.2.0] heptan-6-ones.<sup>6</sup> In our continuing effort to expand the scope of this methodology, we have chosen dimethylene dithioketene for cycloaddition in order to develop a general route for triketo compounds **4** as described in Scheme 1.

In this communication, we report the unusual bond cleavage of silyl ethers **2** in the course of fluoride ion induced fragmentation. Fragmentation reactions of  $\alpha$ -di- and trimethylenedithio group substituted cyclic ketones were previously reported.<sup>7,9,10</sup> Bond cleavage of these precedents occurred consistently at C<sub>6</sub>-C<sub>7</sub> by attack of a nucleophile due to the ring strain and anion stabilizing ability of sulfur atom. However, fragmentation of C<sub>1</sub>-C<sub>7</sub> of compound type **2** were not found in the literature.

Dithiolane-substituted cyclobutanone silyl ethers **2** were prepared by adding 2-chloro carbonyl thiolane (1 eq) to a stirred mixture of corresponding silyl enol ethers (2 eq) and triethylamine in dry ether at room temperature.<sup>11</sup> After usual work-up the cycloadducts **2** were obtained in the yields as described in Table 1.

Interestingly 2-substituted silyl enol ethers (entries **5** and **7**) were inert toward dimethylene dithioketene although they reacted with dichloroketene smoothly.<sup>1</sup> These results together with low yield (24%) of entry **4** might be due to the severe steric repulsion between methyl and thiolane group when the dimethylene dithioketene molecule is twisting from rectangular approaching position to bond forming position.<sup>9</sup> Regiochemistry of the cycloadduct was assigned as described in Table 1 by comparing <sup>1</sup>H and <sup>13</sup>C-NMR spectra of the corresponding dichloroketene cycloadduct<sup>6</sup> and by analyzing <sup>1</sup>H and <sup>13</sup>C-NMR spectra of cleavage products.<sup>10</sup> Stereoselectivity of entries **3** and **4** was also parallel to that of dichloroketene addition products<sup>6</sup> resulting the isomer ratio of exo- and endo- as 27 : 1 and 1 : 1, respectively. Acyclic silyl enol ether (entry **1**) as well as cyclic silyl enol ether underwent cycloaddition smoothly. Comparing yields of cyclic silyl enol ether (entries **2**, **6** and **8**), cycloaddition seemed to be greatly affected by ring conformation. Thus skewed conformation of cyclohexenyl silyl ether (entry **6**) must be building up relatively unfavorable steric environment to the approaching ketene molecule compared to entry **2** and **8**.

When the cycloadducts were treated with *n*-Bu<sub>4</sub>NF in THF at room temperature C<sub>1</sub>-C<sub>7</sub> bond cleavage occurred exclusively resulting 1,3-diketones in almost quantitative yields (Table 1). Any of ring expansion product from C<sub>1</sub>-C<sub>5</sub> bond cleavage was not detectable. Preferential cleavage of C<sub>1</sub>-C<sub>7</sub> bond to C<sub>1</sub>-C<sub>5</sub> bond might be due to overwhelming anion stabilizing ability of thiolane group compared to the driving force of C<sub>1</sub>-C<sub>5</sub> bond cleavage, i.e., ring strain and enolate formation. In an attempt to cleave C<sub>6</sub>-C<sub>7</sub> bond, cycloadducts (entries **2** and **3**) were treated with sodium methoxide in methanol. However, fragmentation occurred in the same fashion as fluoride did. Product resulting from nucleophilic attack on carbonyl group was not obtained. It seemed that transsilylation from silyl ether to methanol occur at first, and then the resulting alkoxide undergo fragmentation as usual pattern.

In summary, salient feature of this work is that dimethylene dithioketene addition to silyl enol ether is new, and due to the fused thiolane group bond cleavage pattern of cyclobutanone was changed from C<sub>1</sub>-C<sub>5</sub> to C<sub>1</sub>-C<sub>7</sub>.

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