scence temperature was not obtained successfully because of thermal decomposition of **1** at above 100℃.

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6. Data: HRMS (70 eV EI, m/z) calcd. for $C_{16}H_{32}FeN_3O_7PSi$: 493.1088. Found: 493.1079. ^{1}H-NMR (δ): 1.32, 1.37 (dd, ^3J=6.0 Hz, Me_2CH, 6H), 2.20 (d, $^3J_{PH}$=10.4 Hz, Me_2N, 9H), 4.85(h, ^3J=6.0 Hz, Me_2CH, 2H). $^{13}C\{^1H\}$NMR (δ): 25.73 (s, Me_2CH), 25.74 (s, Me_2CH), 36.43 (d, $^3J_{PC}$=6.0 Hz, Me_2N), 65.00 (s, Me_2CH), 218.07 (s, CO_{eq}), 221.02 (s, CO_{ap}). $^{29}Si\{^1H\}$NMR (δ): 20.9 (d, $^2J_{PSi}$=25.6 Hz). IR (cm^{-1}): 2007, 1926, 1888 (ν_{CO}, THF soln), 765 (ν_{PN}, KBr pellet).

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

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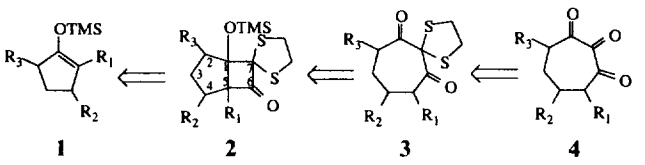
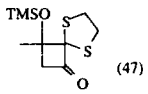
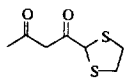
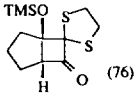
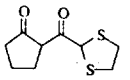
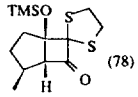
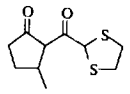
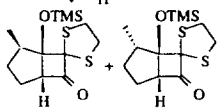
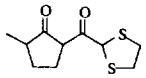
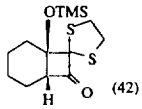
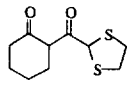
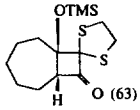
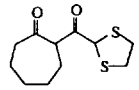
Cycloadducts derive from [2+2] photoaddition[1] or thermal addition[2] have been utilized for the construction of various natural product skeletons.[3] Fragmentation of the cycloadducts was usually performed by ionic and thermal reactions.[4] Radical type fragmentation was also reported.[5] Recently, we reported a ring expansion methodology to prepare substituted cycloheptenones *via* fragmentation of the corresponding 1-trimethylsilyloxy bicyclo [3.2.0] heptan-6-ones.[6] 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.



Scheme 1.

Table 1. Cycloaddition and Fragmentation Products from Silyl Enol Ether

Entry	Silyl enol ethers	Cycloadducts[a,b] (yield %)	Fragmentation products[c,d]
1		 (47)	
2		 (76)	
3		 (78)	
4		 1 : 1	
5		(24) No Reaction	
6		 (42)	
7		No Reaction	
8		 O (63)	

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

In this communication, we report the unusual bond cleavage of silyl ethers **2** in the course of fluoride ion induced fragmentation. Fragmentation reactions of α-di-and trimethylenedithio group substituted cyclic ketones were previously reported.[7,9,10] Bond cleavage of these precedents occurred consistently at C_6-C_7 by attack of a nucleophile due to the ring strain and anion stabilizing ability of sulfur atom. However, fragmentation of C_1-C_7 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 a room temperature.[11] 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.[1] 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.[9] Regiochemistry of the cycloadduct was assigned as described in Table 1 by comparing ^{1}H and ^{13}C-NMR spectra of the corresponding dichloroketene cycloadduct[6] and by analyzing ^{1}H and ^{13}C-NMR spectra of cleavage products.[10] Stereoselectivity of entries **3** and **4** was also paralell to that of dichloroketene addition products[6] 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 envirnment to the approaching ketene molecule compared to entry **2** and **8**.

When the cycloadducts were treated with n-Bu_4NF in THF at room temperature C_1-C_7 bond cleavage occurred exclusiviely resulting 1,3-diketones in almost quantitative yields (Table 1). Any of ring expansion product from C_1-C_5 bond cleavage was not detectable. Preferential cleavage of C_1-C_7 bond to C_1-C_5 bond might be due to overwhelming anion stabilizing ability of thiolane group compared to the driving force of C_1-C_5 bond cleavage, *i.e.*, ring strain and enolate formation. In an attempt to cleave C_6-C_7 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 abtained. 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 cylobutanone was changed from C_1-C_5 to C_1-C_7.

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11. After stirring for 10 hr at room temperature, unreacted starting sily enol ether was recovered. It seemed that reactive dimethylene dithioketene undergo polymerization in the reaction condition. Excess amount of 2-chloro carbonyl thiolane did not affect improvement of yields.
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13. NMR data for cycloadducts and fragmentation products (^{1}H-NMR 300 MHz/$CDCl_3$, ^{13}C-NMR 75 MHz/$CDCl_3$) cycloadducts: Entry **1**. ^{1}H, δ 3.47 (d, J=17.2 Hz, 1H), 3.39-3.17 (m, 4H), 2.97 (d, J=17.2 Hz, 1H), 1.60 (s, 3H) 0.16 (s, 9H); ^{13}C, δ 204.1, 85.0, 72.2, 59.1, 39.5, 37.7, 26.3, 1.7. Entry **2**. ^{1}H, δ 3.64 (d, J=6.9 Hz, 1H), 3.46-3.24 (m, 4H), 2.48 (m, 1H), 2.03-1.83 (m, 4H), 1.59 (m, 1H), 0.22 (s, 9H), ^{13}C, δ 209.7, 84.0, 83.5, 66.5, 39.2, 38.6, 37.5, 29.1, 25.9, 1.8. Entry **3**. ^{1}H, δ 3.45 (m, 1H), 3.37 (s, 1H), 3.34-2.23 (m, 3H), 2.45-2.35 (m, 2H), 2.23 (m, 1H), 1.79 (m, 1H), 1.70 (m, 1H), 1.05 (d, J=7.2 Hz, 3H), 0.24 (s, 9H). ^{13}C, δ 209.1, 84.3, 83.2, 75.6, 39.4, 37.7, 36.8, 35.6, 32.9, 19.5, 1.8. Entry **4**. ^{1}H, δ 3.78 (dd, J=2.7, 8.8 Hz, 0.5H), 3.68 (d, J=7.1 Hz, 0.5H), 3.50-3.01 (m, 4H), 2.28 (m, 1H), 2.00-1.84 (m, 3H), 1.61 (m, 1H), 1.35 (d, J=7.1 Hz, 1.5H), 1.08(d, J=7.0 Hz, 1.5 H), 0.25 (s, 4.5H), 0.22 (s, 4.5H). Entry **6**. ^{1}H, δ 3.72 (dd, J=2.1, 5.7 Hz, 1H), 3.44-3.27 (m, 4H), 2.30 (ddd, J=1.4, 4.0, 13.8 Hz, 1H), 1.96 (ddd, J=1.4, 4.0, 13.8 Hz, 1H), 1.67-1.51 (m, 4H), 1.41 (m, 1H), 1.17 (m, 1H), 0.25 (s, 9H). ^{13}C, δ 206.4, 83.9, 73.2, 62.7, 39.1, 38.0, 36.5, 22.0, 20.6, 19.6, 1.90. Entry **8**. ^{1}H, δ 3.82 (dd, J=5.2, 9.6 Hz, 1H), 3.49-3.19 (m, 4H), 2.15-1.43 (m, 10H), 0.24 (s, 9H). Fragmentation products: Entry **1**. ^{1}H, δ 15.0-13.0 (br s, enolic OH, 0.8H), 5.74 (s, 0.8 H), 4.93 (s, 0.2H), 4.82 (s, 0.8H), 3.78 (s, 0.4H), 3.42-3.26 (m, 4H), 2.25 (s, 0.6 H), 2.15 (s, 2.4H). Entry **2**. ^{1}H δ 13.31 (s, enolic OH, 0.67H), 5.40 (s, 0.33H), 4.99 (s, 0.67H), 3.76 (t, J=7.0 Hz, 0.33H), 3.52-3.29 (m, 4H), 2.67-1.94 (m, 6H). Entry **3**. ^{1}H, δ 13.50 (br s, enolic OH, 0.69H), 5.34 (s, 0.69H), 5.03 (s, 0.31H), 3.56 (m, 0.31H), 3.41-3.10 (m, 4H), 2.73-2.18 (m, 4H), 1.70-1.45 (m, 1H), 1.20 (d, J=7.0 Hz, 0.93H), 1.14 (d, J=7.0 Hz, 2.07H). Entry **4**. Since ^{1}H-NMR spectra is so complex as expected due to an equilibrium mixture of various enolic forms along with diastereomevic isomers that only a few characteristic peaks are listed. ^{1}H, δ 13.50 (br s, enolic OH), 5.42, 5.41, 4.99, and 4.97 (singlets, 1H). Entry **6**. ^{1}H, δ 15.30 (s, 0.86H), 5.23(s, 0.86H), 5.03 (s, 0.14H), 3.90 (dd, J=2.7, 8.9 Hz, 0.14H), 3.49-3.22 (m, 4H), 2.53-2.36 (m, 4H), 1.74-1.69 (m, 4H). Entry **8**. ^{1}H, δ 16.34 (s, 0.86H), 5.38 (s, 0.86H), 5.07 (s, 0.14H), 4.03 (dd, J=4.1, 10.6 Hz, 0.14H), 3.51-3.28 (m, 4H), 2.57 (m, 2H), 2.44 (m, 2H), 1.19-1.37 (m, 6H).