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Reaction of Acylsilanes with Sulfur Ylides. Selective Formation of Silyl Enol Ethers or β-Ketosilanes.

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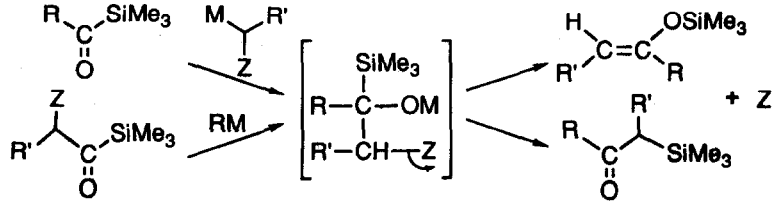
Abstracts : *The reaction of acylsilanes with sulfur ylides in THF results in the formation of the corresponding silyl enol ethers or β-ketosilanes. The relative ratio of these products varies with the ylide conditions and the stability of ylide used. It is noteworthy that silyl enol ethers were formed under the salt-free ylide conditions, and that β-ketosilanes were yielded in the presence of soluble inorganic salts in THF, selectively. The formation of both products would be interpreted in terms of the anionotropic and cationotropic rearrangements of silyl group in the reaction intermediate.*

Recent progress achieved by using acylsilanes has offered several new aspects to synthetic organic chemistry[1] and has been reviewed in detail by Ricci and Degl'Innocenti.[1d] Of special interest to us are migratory behaviors of silyl group in the reaction of acylsilanes with organometallic reagents. For examples, Reich and coworkers have described interesting transformation of these ketones, in which α-silyl alkoxides derived from acylsilanes and suitable organolithium undergo Brook rearrangements to the isomeric silyloxy carbanions, being isolated as silyl enol ethers.[2] Kuwajima et al. observed that α-silyl alkoxides derived from (α-chloroacyl)silanes and alkylmagnesium halides suffer silyl migration from C to C, giving the corresponding β-ketosilanes.[3] In these reactions, the nature of the leaving group (Z) in the β-position of α-silyl alkoxides has been considered to control the balance between the migration of silyl group to O and that to C (Scheme 1).[2] Prior to these observations, Brook et al. reported that the reaction of benzoylsilane with alkylidene phosphoranes gave silyl enol ethers,[4a] and that the reaction of acylsilanes with diazomethane gave silyl enol ethers and the homologous β-ketosilanes.[4]

Scheme 1.



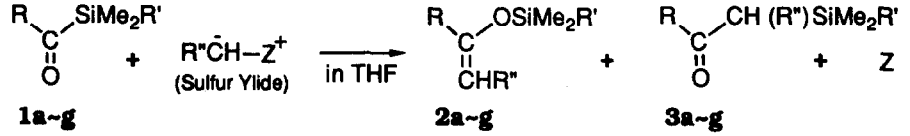
The formation of silyl enol ethers in the above reactions implies 1,2-migration of silyl group as a cationic moiety (cationotropy), whereas that of β-ketosilanes refers to 1,2-migration of silyl group as an anionic moiety (anionotropy) in the intermediate. Compared with the well-known Brook rearrangement (cationotropy) of silicon,

such anionotropic rearrangements of silyl group have been hardly applied to organic synthesis since there were no suitable methods to generate the required intermediates in a more practical manner.[5]

The migratory aptitude of silyl group mentioned above prompted us to investigate the reaction of acylsilanes with sulfur ylides. Although sulfur ylides have been well known to interact with aldehydes and ketones to afford epoxides,[6] the sulfur ylides in the reacion with acylsilanes are expected to function in a manner comparable to diazomethane because a comparison of sulfur ylides and diazo compounds shows a striking resemblance in terms of both structure and reactivity.[6b]

Previously we reported a preparation of a series of new cyclopropylacylsilanes.[7] As a part of the study to clarify their chemical behavior and synthetic utility, we disclose in this paper that the reaction of various acylsilanes (**1**) involving new cyclopropylacylsilanes with sulfur ylides affords the corresponding silyl enol ethers (**2**) and the homologous β-ketosilanes (**3**), and that the relative ratio of these products can be controlled under the appropriate reaction conditions.

Scheme 2.



1a~g **2a~g** **3a~g**

	a	b	c	d	e	f	g
R	-- substituted cyclopropyl --				Ph	$PhCH_2$	C_8H_{17}
R'	------- Me, t-Bu, or Ph ---------						
R"	---------- H or Me ----------						

$R"\bar{C}H-Z^+$	R"	Z
DMSY	H	$Me_2S(O)$
DTSY	H	*p*-tolyl-S(O)NMe_2
DPSY	H or Me	Ph_2S

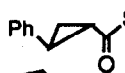
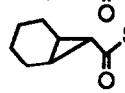
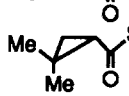
Results and Discussion

Acylsilanes and Sulfur Ylides. Although a number of effective procedures is now available for the preparation of many types of acylsilanes,[8] only five synthetic routes to cyclopropylacylsilanes have been reported.[7,9] A series of cyclopropylacylsilanes used here was prepared from 1-lithio-1-silylcyclopropanes and dichloromethyl methyl ether.[7] Some simple acylsilanes were prepared by the reported methods.[10] Sulfur ylides used here are dimethyloxosulfonium methylide (DMSY), (dimethylamino)-*p*-tolyloxosulfonium methylide (DTSY), and dipheylsulfonium methylide or ethylide (DPSY), prepared from the corresponding oxosulfonium or sulfonium salts (halide and tetrafluoroborate), according to the methods of Corey [6a] and Johnson.[11]

Reaction of Acylsilanes with Dimethyloxosulfonium Methylide (DMSY). Acylsilanes (**1**) were allowed to react with a small excess of dimethyloxosulfonium methylide (DMSY) in THF. The reaction mixture was treated with pentane containing small amounts of water to give a mixture of the corresponding silyl enol ethers (**2**) and the homologous β-ketosilanes (**3**). Gas chromatographic analysis of the crude product showed there was no detectable amount of epoxysilanes. These products (**2** and **3**) were isolated by bulb-to-bulb distillation *in vacuo* and their structures were determined by Mass analysis, IR and NMR spectroscopies. The relative ratio of **2** and **3** was determined by gas chromatography below 160°C to avoid the thermal isomerization of **3** to **2**.[12a,b] Column chromatography (on silica gel or alumina) could not be used for isolation of products in this study, except for some cases, because the use of this technique resulted in the formation of the corresponding methyl ketones by protiodesilylation of **2** or **3**.[12c,d, 13]

Table 1 gives the conditions and results of the reaction of various acylsilanes with DMSY generated from trimethyloxosulfonium iodide and n-butyllithium in THF at 20 or -80°C. The total yields of the products were ex-

Table 1. Reaction of Acylsilanes with Dimethyloxosulfonium Methylide (DMSY)[a]

Acylsilane 1		Temp (°C)	Products and relative ratio[b] 2	(%)	3	(%)	Total yield[b] (%)
	**1a**	20	**2a**	13	**3a**	87	81
		-80		43		57	73
	**1b**	20	**2b**	18	**3b**	82	84
		-80		70		30	83
	**1c**	20	**2c**	5	**3c**	95	85
		-80		19		81	85
	**1d**	20	**2d**	18	**3d**	82	72
		-80		66		34	85
	**1e**	20	**2e**	65	**3e**	35	83
		-80		86		14	60
	**1f**	20	**2f**	10	**3f**	90	90
		-80		86		14	91

a) Molar ratio **1** : DMSY : THF = 1 : 1 : 250. DMSY was generated from $Me_3S^+(O)I^-$ and BuLi (salt-containing ylide). Reaction time 2h. b) Determined by GC.

cellent (80~90%) and the ratios of **2** and **3** were strongly dependent upon the reaction temperature. At 20°C, the preferential formation of **3** was observed, except for the reaction of **1e**. On the other hand, when the reaction was conducted at -80°C, the ratio of **2** to **3** was enhanced and an inversion of the ratio was observed in some cases (**1b**, **1d**, and **1f**). The above results can not be rationalized on the assumption that the change in reaction temperature led to an alteration in the relative reaction rates to **2** and **3** from **1**, or caused a displacement of the enol-keto equilibrium between **2** and **3**, since the both reaction rates to **2** and **3** were very rapid even at -80°C and the interconversion between **2** and **3** was not observed under these reaction conditions as mentioned later.

Taking into account that the ylide solution used here contains lithium iodide and that the solubility of inorganic salts to THF is highly dependent on temperature, an effort was then made to compare the results of the reaction in which no lithium salts were present with those when lithium iodide is present in the reaction mixture. The salt-free ylide in THF was prepared by the reaction of trimethyloxosulfonium chloride with sodium hydride followed by removing of sodium chloride which is almost insoluble in THF even at room temperature.[6a] Table 2 shows the results under the salt-free conditions (**A**) and those obtained by using the salt-containing ylide solution (**B**) prepared by addition of equimolar lithium iodide to the above salt-free ylide solution. In the reaction under the salt-free conditions (**A**) at 20°C, silyl enol ethers (**2**) were preferentially formed and the ratios of **2** to **3** in all cases were greater (70~99/30~1) than those from the reaction at -78°C in Table 1. On the contrary, when the reaction was conducted in the presence of lithium iodide at 20°C (**B**), the ratios of **2** to **3** produced were 11~19/89~91, except for the case of benzoylsilane (**2** : **3** = 66 : 34). These results are comparable to those found for the case where the reaction with the ylide generated using n-butyllithium was carried out at 20°C (see Table 1). Thus, the absence or presence of lithium salt appears to play an important role in determining the ratio of **2** to **3** produced.

We also examined the effects of salts and solvents on the product ratio in the reaction of 2,2-dimethylcyclopropyl trimethylsilyl ketone (**1d**) with DMSY. Although an equimolar amount of salts to DMSY was added to the salt-free DMSY solution in this experiment, the concentration of salts dissolved in the DMSY solution was found to differ depending upon the kind of salts and solvents. Table 3 shows that the product ratio was highly

Table 2. Reaction of Acylsilanes with Salt-free Dimethyloxosulfonium Methylide (DMSY) [a] and Effect of Additive Lithium Iodide

Acylsilane 1	Ylide conditions[b]	Products and relative ratio[c] 2	(%)	3	(%)	Total yield[c] (%)
1a	**A**	**2a**	89	**3a**	11	73
	B		12		88	77
1b	**A**	**2b**	96	**3b**	4	75
	B		19		81	92
1c	**A**	**2c**	79	**3c**	21	95
	B		13		87	80
1d	**A**	**2d**	70	**3d**	30	75
	B		18		82	70
1e	**A**	**2e**	99	**3e**	—	71
	B		66		34	91
1f	**A**	**2f**	91	**3f**	9	45
	B		11		89	62

a) DMSY was generated from $Me_3S^+(O)Cl^-$ and NaH; Reaction temp. 20°C; Reaction time 2h. b) Ylide conditions **A** : Salt-free ylide was used ; Molar ratio **1** : DMSY : THF = 1 : 1 : 250. **B** : LiI was added to salt-free DMSY ; Molar ratio **1** : DMSY : LiI : THF = 1 : 1 : 1 : 250. c) Determined by GC.

dependent upon the solubility of salts in DMSY solution. The presence of soluble salts such as LiI and $LiBF_4$ in THF or dioxane resulted in the preferencial formation of **3**, whereas **2** was preferentially formed when inorganic salts are dissolved in low concentration in the DMSY solution, such as NaI and KI in THF or LiI in ether.[14]

As can be seen from the results cited on Tables 1 and 2, alterations in the structure of acyl group of **1** were not so effective on the reactivity and the products distribution in these reactions. Benzoylsilane (**1e**) was exceptionally liable to form silyl enol ether compared with other alkylacylsilanes. In attempt to elucidate the effect of the silyl substituents of **1** on the product distribution, we have employed a series of 2,2-dimethylcyclopropylacylsilanes (**1d**, **1d-b**, and **1d-p**) bearing different type of silyl group, and the results were summarized in Table 4. Again, the reaction under the salt-free conditions resulted in the predominant formation of **2** in all cases. When the reaction was conducted in the presence of salt, the ratio of **3** to **2** produced was enhanced in the reaction of

Table 3. Effect of Additive Salts and Solvents on Reaction of 2,2-Dimethylcyclopropyl Trimethylsilyl Ketone (**1d**) with DMSY [a]

Solvent	Additive salt (Solubility mol/L)[b]		Temp (°C)	Products and relative ratio[c] **2d** (%)	**3d** (%)	Total yield[c] (%)
THF	LiI	(2.0×10^{-1})	20	18	82	70
	NaI	(1.3×10^{-1})	20	71	29	49
	KI	(4.9×10^{-2})	20	86	14	52
	$LiBF_4$	(2.1)	20	8	92	65
Ether	LiI	(2.9×10^{-3})	35	93	7	38
Dioxane	LiI	(4.2×10^{-1})	20	4	96	97

a) Molar ratio **1d** : DMSY : Salt : THF = 1 : 1 : 1 : 250. DMSY (salt-free) was generated from $Me_3S^+(O)Cl^-$ and NaH. Reaction time 2h. b) Solubility of each salt was determined by measuring the amount of salt dissolved in the DMSY solution at 20°C. c) Determined by GC.

Table 4. Effect of Silyl Substituents on Reaction of 2,2-Dimethylcyclopropyl-acylsilanes with DMSY [a]

1 (Si =)		Ylide conditions[b]	Temp (°C)	Time (h)	Products and relative ratio[c] 2	(%)	3	(%)	Total yield[c] (%)
1d	($SiMe_3$)	**A**	20	1	**2d**	70	**3d**	30	75
		B	20	1		18		82	70
1d-b	($SiMe_2Bu$)	**A**	45	4	**2d-b**	95	**3d-b**	5	44
		B	45	3		5		95	65
1d-p	($SiMe_2Ph$)	**A**	20	1	**2d-p**	99	**3d-p**	trace	84
		B	20	1		45		55	92

a) DMSY (salt-free)was generated from $Me_3S^+(O)Cl^-$ and NaH; Reaction temp. 20°C. b) Ylide conditions **A** : Salt-free ylide was used ; Molar ratio **1** : DMSY : THF = 1 : 1 : 250. **B** : LiI was added to salt-free DMSY ; Molar ratio **1** : DMSY : LiI : THF = 1 : 1 : 1 : 250. c) Determined by GC.

1d-b bearing t-butyl group on silicon, while the ratio was reduced in that of **1d-p** having phenyl group on silicon, compared with the result from **1d**.

Reacion of Acylsilanes with (Dimethylamino)-*p*-tolyloxosulfonium Methylide (DTSY) . In order to elucidate the scope of this reaction, we next examined the behavior of some other sulfur ylides, being less stable than dimethyloxosulfonium methylide. Salt-free and salt-containing (dimethylamino)-*p*-tolyloxosulfonium methylides (DTSY) were prepared by the treatment of (dimethylamino)-methyl-*p*-tolyloxosulfonium tetrafluoroborate with sodium hydride and butyllithium respectively, and were allowed to react with acylsilanes in THF at 20°C. The results were summarized in Table 5. The reaction under the salt-free conditions proceeded somewhat sluggishly to give significant amounts of the corresponding methyl ketones (**4**) in addition to a mixture of **2** and **3**. The formation of methyl ketones (**4**) seems to be mainly due to the protiodesilylation of **2** in the step

Table 5. Reaction of Acylsilanes with (Dimethylamino)-*p*-tolyloxosulfonium Methylide (DTSY) [a]

Acylsilane 1	Ylide conditions[a]	Time (h)	Products and relative ratio[b] 2	(%)	3	(%)	4[c]	(%)	Total yield[b] (%)
1b	**A**	4	**2b**	–	**3b**	8	**4b**	92	48
	B	1		–		>99		–	75
1c	**A**	1	**2c**	–	**3c**	2	**4c**	98	68
	B	2		–		>99		–	75
1d	**A**	6	**2d**	77	**3d**	23	**4d**	–	34
	B	7		2		98		–	27
1e	**A**	2	**2e**	19	**3e**	–	**4e**	81	30
	B	1		16		84		–	45
1f	**A**	5	**2f**	10	**3f**	4	**4f**	86	5
	B	1		2		98		–	70

a) **A** : Reaction was carried out under salt-free conditions. Salt-free DTSY was generated from *p*-Me-C_6H_4-$S^+(O)(NMe_2)Me$ BF_4^- and NaH, and the resulting $NaBF_4$ was removed. Molar ratio ; **1** : DTSY : THF = 1: 1.1 : 250. Reaction temp. 20°C. **B** : Reaction was carried out in the presence of salt. DTSY was generated from *p*-Me-C_6H_4-$S^+(O)(NMe_2)Me$ BF_4^- and BuLi. Molar ratio ; **1** : DTSY : $LiBF_4$: THF = 1: 1.1 : 1 : 250. Reaction temp. 20°C. b) Determined by GC. c) **4** : The corresponding methyl ketones, **R-CO-Me**.

of work-up.[12,13] On the other hand, the reactions in the presence of salt (lithium tetrafluoroborate) resulted in the almost exclusive formation of **3**, except for the case of benzoylsilane (**1e**) even in which the relative ratio of **3e** to **2e** was remarkably enhanced in comparison with that in the reaction using DMSY (see Tables 1 and 2). Thus, the presence of inorganic salt seems to be useful for the selective formation of **3**. The lower reactivity of DTSY compared with DMSY may be due to the bulkiness of substituent on sulfur atom.

Reacion of Acylsilanes with Diphenylsulfonium Methylide and Ethylide (DPSY). Diphenylsulfonium methylide and ethylide were prepared by the treatment of diphenylmethyl- and diphenylethylsulfonium tetrafluoroborate with t-butyllithium respectively, and were allowed to react with acylsilanes at -80°C in the presence of lithium tetrafluoroborate because these ylides were less stable than oxosulfonium ylides (see Figure 3 in experimental section). Results were summarized in Table 6. The reaction of cyclopropylacylsilanes (**1c, d**) or benzoylsilane (**1e**) led to the exclusive formation of the corresponding β-ketosilanes (**3**) in spite of the low reaction temperature, while the similar treatment of benzyl or octylacylsilane (**1f** or **1g**) afforded a mixture of **3** and significant amounts of the corresponding epoxysilanes (**5**).

Table 6. Reaction of Acylsilanes with Diphenylsulfonium Methylide and Ethylide (DPSY)[a]

Acylsilane	$Ph_2\overset{+}{S}\overset{-}{C}HR'$	Products and relative ratio[b]						Total yield[b]
1	R'	**2**	(%)	**3**[c]	(%)	**5**[d]	(%)	(%)
1c	H	–		**3c**	>99		–	84
	CH_3	–		**3c-m**	>99		–	76
1d	H	–		**3d**	>99		–	96
	CH_3	–		**3d-m**	>99		–	85
1e	H	–		**3e**	>99		–	76
	CH_3	–		**3e-m**	>99		–	84
1f	H	–		**3f**	78	**5f**	22	72
	CH_3	–		**3f-m**	38	**5f-m**	62	55
C_8H_{17}-C(=O)-$SiMe_3$ **1g**	H	–		**3g**	64	**5g**	36	80
	CH_3	–		**3g-m**	37	**5g-m**	63	99

a) DPSY was generated from $Ph_2S^+CH_2R'BF_4^-$ and t-BuLi; Reaction was carried out in the presence of $LiBF_4$. Molar ratio **1** : DPSY : THF = 1 : 1 : 250. Reaction temp. -80°C. Reaction time 2h. b) Determined by GC.

c) **3-m** : R-C(=O)-C(OMe)HSiMe$_3$ d) **5** : R-C(SiMe$_3$)(O)-CH$_2$ **5-m** : R-C(SiMe$_3$)(O)-CHMe

Mechanistic Aspects. In addition to the thermal isomerization of β-ketosilanes to the corresponding silyl enol ethers,[12] silyl enol ethers bearing a sterically hindered silyl group rearrange to β-ketosilanes in the presence of n-butyllithium and potassium t-butoxide.[15] In connection with such findings, some efforts were made to confirm the possibility of interconversion between **2** and **3** produced under the acylsilane/sulfur ylide reaction conditions. A mixture of **2d** and **3d** was treated with DMSY solution containing lithium iodide, and a fraction of the mixture was taken out at regular time intervals followed by GC analysis. The relative ratio of **2d** and **3d** in the reaction mixture, as shown in Figure 1, remained unchanged over a period of 3 h, though both compounds used were somewhat consumed at the initial stage of treatment to give the corresponding methyl ketone (**4d**) produced by the protiodesilylation. This observation indicates that no interconversion occurred between **2** and **3** produced in the acylsilane/sulfur ylide reaction.

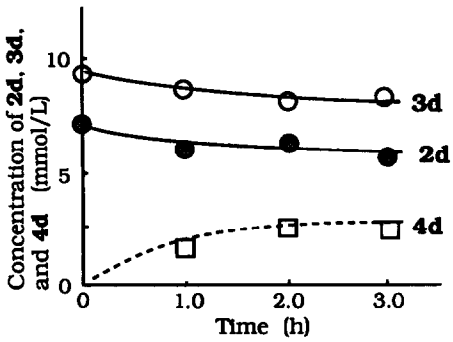


Figure 1. Treatment of the mixuture of **2d** and **3d** with DMSY at 25°C.
[Initial molar ratio ; **2d** : **3d** : DMSY : THF = 0.7 : 0.9 : 0.8 : 250]

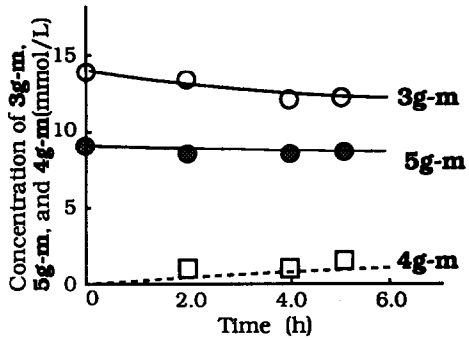
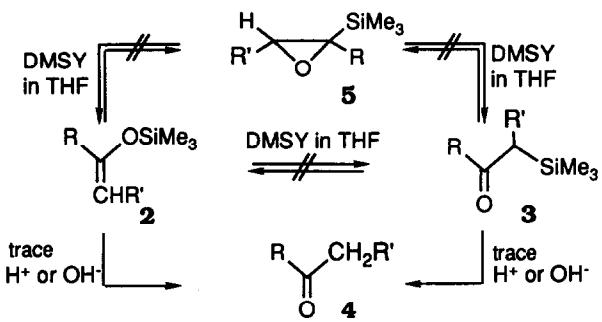


Figure 2. Treatment of the mixuture of **3g-m** and **5g-m** with DMSY at 25°C.
[Initial molar ratio ; **3g-m** : **5g-m** : DMSY : THF = 1.4 : 0.9 : 1.1 : 250]

It has been well known that sulfur ylides react with carbon analogues of acylsilanes to give the corresponding epoxides,[6] and that epoxysilanes undergo rearrangement when treated with magnesium halide to afford the corresponding β-ketosilanes or silyl enol ethers depending on reaction conditions.[16] These facts may suggest an intermediary formation of epoxysilanes (**5**) and the subsequent rearrangement to **2** or **3** from **5** in our acylsilane/sulfur ylide reaction. To make sure this possibility, a mixture of **3g-m** and **5g-m** was treated with DMSY solution containing salt. Figure 2 suggests that the relative ratio of **3g-m** and **5g-m** in the mixture remained almost constant throughout 6 h at 25°C although a part of these compounds were consumed to afford the protiodesilylation product (**4**). Thus, this result indicates that there was no intermediary formation of **5** in our acylsilane/sulfur ylide reaction (Scheme 3).

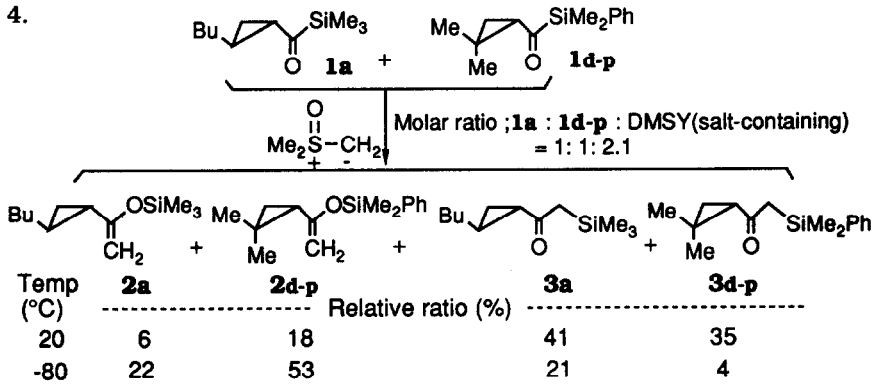
Scheme 3.



Further, crossover experiments suggest that the formation of **2** and **3** in the acylsilane/sulfur ylide reaction involves an intramolecular migration of silyl group; when an equimolar mixture of 2-butylcyclopropyl trimethylsilyl and 2,2-dimethylcyclopropyl dimethylphenylsilyl ketones (**1a** and **1d-p**) was treated with DMSY in the presence of LiI at 20° or -80°C, the corresponding silyl enol ethers and β-ketosilanes (a mixture of **2a**, **2d-p**, **3a**, and **3d-p**) were obtained with no crossover products which can be detected by GC analysis of the crude reaction mixture (Scheme 4).

Johnson and coworkers have suggested that betaines are intermediates in the nucleophilic methylene transfer reaction of sulfonium ylides to carbonyl groups.[11b] Furthermore, it has been known that the organosilyl group undergoes anionotropic 1,2-rearrangement (C to C rearrangement of a silyl group as an anionic moiety) in addition to cationotropic 1,2-migration (C to O migration of a silyl group as a cationic moiety; Brook rearrange-

Scheme 4.



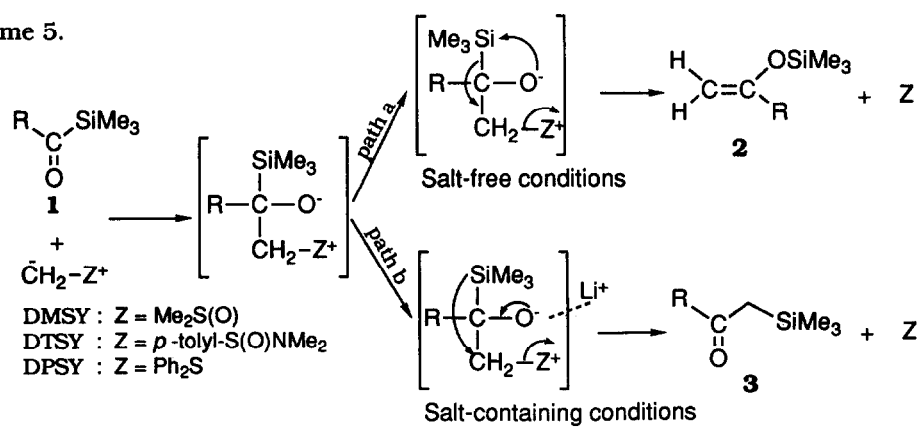
Temp (°C)	2a	2d-p	3a	3d-p
	Relative ratio (%)			
20	6	18	41	35
-80	22	53	21	4

ment),[4,5] as mentioned above.

Thus, the reaction of acylsilanes with sulfur ylides can be interpreted to proceed through the initial formation of a betaine intermediate, followed by discrete silyl migrations (path a and b) as represented in Scheme 5. A cationotropic rearrangement of silyl group to the oxyanion on the carbon adjacent to silicon in the intermediate, followed by the elimination of neutral sulfur compounds (Z), leads to the formation of silyl enol ethers (2) (path a). Alternatively, an anionotropic migration of silyl group to the electron-deficient center (CH_2), accompanied by the elimination of Z, results in the formation of β-ketosilanes (3) (path b). These silicon migrations in the intermadiate are considered to occur much faster than the attack of oxyanion to the electron-deficient center, forming epoxide ring, because pentacoordinate transition states using vacant *d* orbitals are possible in silicon.[1a,17]

In the reaction under the salt-free conditions, the naked oxyanion may rapidly attack silicon (cationotropy of silyl group) to afford 2. The preferential formation of 3 in the reaction in the presence of lithium salt is rationalyzed in view that the tight ion pair between oxyanion in the intermediate and lithium cation prevents the formation of Si-O bond and assists the anionotropy of silicon to the electron-deficient center.

Scheme 5.



When the reaction in the presence of salt was carried out at low temperature, the lithium salt would be precipitated due to the low solubility of salt in THF at that temperature.[14] Thus the reaction with DMSY generated using n-butyllithium at -80°C (Table 1) seems to proceed just as that under salt-free conditions to give 2 predominantly.

As shown in Tables 4 and 5, the behavior of oxosulfonium ylides (DMSY and DTSY) and sulfonium ylides (DPSY) was considerably different in the reaction in the presence of lithium salt. The reaction with the former ylides gave a mixture of β-ketosilanes (3) and small amounts of silyl enol ethers (2), whereas that with the latter was liable to form only 3, or epoxysilanes (5) in addition to 3 in some cases. This distinction could be attributed to elimination of sulfide (R_2S) being easier than that of sulfoxide (R_2S=O) from the corresponding betaine intermediate. Although we have no information on the leaving aptitude of sulfur compounds from the intermediates, this aptitude is considered to be consistent with the ease of spontaneous thermal decomposition of ylides. The stability against the thermal decomposition of ylides decreases in the following order ; DMSY > DTSY >> DPSY (see Figure 3 in experimental section). Thus, the good leaving aptitude of R_2S compared with R_2S=O would enhance the cationic character of the methylene carbon, transfered from the ylide, in the betaine intermediate, and accelerate the anionotropy of silyl group towards the cationic site to yield β-ketosilane selectively.

The effect of the group on carbonyl carbon of **1** against both processes in this reaction parallels closely that proposed for the reaction of acylsilanes with diazomethane.[4b,c] The process to silyl enol ethers occurs most readily when the group (phenyl or 2-phenylcyclopropyl) on carbonyl carbon of **1** is able to delocalize the negative charge on the carbon, which is developed by migration of silicon to oxyanion (cationotropy of silicon). Alternatively, β-ketosilanes (3) are the major product when the carbonyl carbon is substituted with electron releasing alkyl group which would tend to increase electron density on the carbon and thus to disfavor cationotropy of silicon in the intermediate. In the latter case, the use of highly reactive sulfur ylide (DPSY in this case) would result in the competitive reaction between the attack of oxyanion and the anionotropy of silyl group to the electron deficient center in the intermediate, forming **5** in addition to **3**. The presence of electron releasing alkyl group on silicon of **1** also seems to enhance the anionic character of silyl group and to assist the anionotropy to yield 3.

Conclusion. It has been shown that the reaction of acylsilanes with sulfur ylides in THF resulted in the formation of the corresponding silyl enol ethers or β-ketosilanes, and that the relative ratio of both compounds could be controlled by the absence or presence of soluble inorganic salt in the reaction system. The reaction under the salt-free conditions proceeded accompanying cationotropic rearrangement of silicon in the reaction intermediate to form the corresponding silyl enol ethers, and β-ketosilanes were formed selectively by the reaction in the presence of soluble inorganic salts, which proceeded accompanying anionotropic migration of silicon. Especially, the latter reaction could be a useful and practical manner for the anionotropy of silicon.[18]

Experimental Section

General Procedures. Infrared (IR) spectra were taken on a JASCO A-202 spectrometer. Proton nucler magnetic resonance (^{1}H-NMR) spectra were measured in $CDCl_3$ on a JEOL-JNM-FX-100 (100MHz) or GX-400 (400 MHz) spectrometer. Unless otherwise noted, ^{1}H-spectra were taken at 100 MHz. ^{13}C-NMR spectra were measured in $CDCl_3$ at 25 MHz on a JEOL-JNM-FX-100. Chemical shifts were expressed in parts per milion (δ) down field from internal tetramethylsilane. Mass spectra were determined on a Hitachi M-80 instrument at 20 or 70 (HRMS) eV ionizing irradiation. UV spectra were recorded on a Hitachi 200-10 spectrophotometer. Analytical gas-liquid chromatography (GC) was performed on a Shimadzu GC-14A instrument with a flame ionization detector using a Silicon OV-1 (1% on Shimalite W, 2m) column.

All reactions using alkyllithium reagents and ylides were performed in flame-dried glassware under a positive pressure of argon or nitrogen. Reaction mixtures were stirred magnetically. Solutions of alkyllithium reagents and ylides were transferred by syringe or cannula and were introduced into reaction vessels through rubber septa. Solutions of n-butyllithium and t-butyllithium were titrated with 2,5-dimethoxybenzyl alcohol. Tetrahydrofuran (THF) was distilled from potassium benzophenone ketyl in a recycling still immediately before use.

Column chromatography was performed on Fuji-Devison silica gel BW127-ZH (200 mesh).

General Procedure for the Preparation of Cyclopropylacylsilanes.[7] To a solution of the readily available 1-bromo-1-trimethylsilylcyclopropanes[19] (10 mmol) in THF (30mL) was added n-butyllithium (11 mmol) in hexane dropwise at -95~-100°C. The resulting solution was stirred for 20 min. The lithiocyclopropanes thus obtained were treated with dichloromethyl methyl ether (12~15 mmol) in THF (5mL) dropwise at -95°C. After being stirred for 2 h, methanol (2 mL) was added to the mixture at the same temperature. The resulting mixture was then allowed to come to room temperature and poured into brine and the products were extracted several times with ether. The combined ether layers were washed to neutrality with brine, dried over sodium sulfate, and concentrated *in vacuo*. The residue was subjected to column chromatography using hexane and then ether eluents. The ether fraction was concentrated and distilled to afford the corresponding cyclopropylacylsilanes (**1**) in 30~50% yield. In this preparation, **1a** and **1c** were obtained as *exo* isomer with 95% purity. Although **1b** was obtained as a mixture of *exo* and *endo* isomer, the treatment of the *exo* and *endo* mixture with dilute HCl at room temperature for a few minutes gave only *exo*-**1b** (*endo*-**1b** was converted into the *exo*-isomer).

The physical data of new cyclopropylacylsilanes are as follows.

2-Butylcyclopropyl Trimethylsilyl Ketone (1a). bp: 35°C (0.1 mmHg). ^{1}H-NMR (400 MHz): *exo* isomer δ 0.23 (s, 9H), 0.69~0.72 (m, 1H), 0.88 (t, *J*=5.6 Hz, 3H), 1.24~1.27 (m, 1H), 1.28~1.39 (m, 6H), 2.19~2.27 (m, 2H). ^{13}C-NMR: *exo* isomer δ -3.2 (q, $^1J_{CH}$=120 Hz), 13.96 (q, $^1J_{CH}$= 124 Hz), 18.43 (t, $^1J_{CH}$=162 Hz), 22.27 (t, $^1J_{CH}$= 126 Hz), 27.22 (d, $^1J_{CH}$= 162 Hz), 31.40 (t, $^1J_{CH}$=126 Hz), 33.16 (t, $^1J_{CH}$=129 Hz), 33.63 (d, $^1J_{CH}$=162 Hz), 245.82(s). UV: n→π* λmax (ε) 371(94) nm. IR (neat): 2975, 1620, 1460, 1390, 1250, 1060, 1040, 840 cm^{-1}. MS: m/e (relative intensity) 198 (M$^+$, 13%), 183 (34), 155 (100), 141(63), 127 (48), 99 (73), 75 (99), 73(99). HRMS: Found M$^+$, 198.1430. $C_{11}H_{22}SiO$ requires M, 198.1439.

2-Phenylcyclopropyl Trimethylsilyl Ketone (1b). bp: 70°C (0.15 mmHg). ^{1}H-NMR: *exo* isomer δ 0.24 (s, 9H), 1.35 (ddd, *J*=7.9, 6.4, 4.0 Hz, 1H), 1.70 (ddd, *J*=8.8, 5.2, 4.0 Hz, 1H), 2.52 (ddd, *J*=8.8, 6.4, 4.0 Hz, 1H), 2.74 (ddd, *J*=7.9, 5.2, 4.0 Hz, 1H), 7.09~7.30 (m, 5H). ^{13}C-NMR: *exo* isomer δ -3.4 (q, $^1J_{CH}$= 120 Hz), 19.0 (t, $^1J_{CH}$=169 Hz), 29.5 (d, $^1J_{CH}$=169 Hz), 36.9 (d, $^1J_{CH}$=162 Hz), 126.0 (d, $^1J_{CH}$=161 Hz), 127.6 (d, $^1J_{CH}$=159 Hz), 128.3 (d, $^1J_{CH}$=157 Hz), 140.5 (s), 244.4 (s); *endo* isomer δ -3.7 (q, $^1J_{CH}$=120 Hz), 10.6 (t, $^1J_{CH}$= 169 Hz), 29.8 (d, $^1J_{CH}$= 169 Hz), 34.4 (d, $^1J_{CH}$= 162 Hz), 126.2 (d, $^1J_{CH}$= 161 Hz), 127.6 (d, $^1J_{CH}$= 159 Hz), 128.8 (d, $^1J_{CH}$= 157 Hz), 135.8 (s), 242.8 (s). UV: n→π* λmax (ε) 369 (108) nm. IR: 3020, 2990, 1630, 1510, 1460, 1362, 1060, 898, 850, 760, 700 cm^{-1}. MS: m/e (relative intensity) 218 (M$^+$, 34%), 203 (15), 129 (7), 104 (70), 99 (9), 75 (24), 73 (100). HRMS: Found M$^+$, 218.1135. $C_{13}H_{18}SiO$ requires M, 218.1127.

7-Bicyclo[4.1.0]heptyl trimethylsilyl ketone (1c). bp: 69°C (1.5 mmHg). ^{1}H-NMR (400 MHz): *exo* isomer δ 0.22 (s, 9H), 1.20~1.35 (m, 4H), 1.63~1.76 (m, 4H), 1.85~1.93 (m, 2H), 2.30 (seemingly t, *J*=4.3 Hz, 1H). ^{13}C-NMR: *exo* isomer δ -3.4 (q, $^1J_{CH}$=120 Hz), 21.0 (t, $^1J_{CH}$=126 Hz), 23.2 (t, $^1J_{CH}$=123 Hz), 26.3 (d, $^1J_{CH}$=163 Hz), 40.4 (d, $^1J_{CH}$=163 Hz), 245.1 (s). UV: n→π* λmax (ε) 365 (68) nm. IR (neat): 2950~2850, 1620, 1450, 1405, 1255, 1055, 845 cm^{-1}. MS: m/e (relative intensity) 196 (M$^+$, 9%), 181 (16), 167 (15), 130 (10), 99 (11), 75 (23), 73(100). HRMS: Found M$^+$, 196.1279. $C_{11}H_{20}SiO$ requires M, 196.1283.

2,2-Dimethylcyclopropyl trimethylsilyl ketone (1d). bp: 64°C (18 mmHg). ^{1}H-NMR (400 MHz): δ 0.21 (s, 9H), 0.74 (dd, *J*=7.3, 4.0 Hz, 1H), 0.96 (s, 3H), 1.25 (s, 3H), 1.45 (dd, *J*=5.8, 4.0 Hz, 1H), 2.43 (dd, *J*= 7.3, 5.8 Hz, 1H). ^{13}C-NMR: δ -3.6 (q, $^1J_{CH}$=122 Hz), 18.3 (q, $^1J_{CH}$= 129 Hz), 22.2 (t, $^1J_{CH}$=155 Hz), 27.3 (q, $^1J_{CH}$=124 Hz), 28.2 (s), 40.5 (d, $^1J_{CH}$=156 Hz), 245.3 (s). UV: n→π* λmax (ε) 371 (124) nm. IR (neat): 2945, 1620, 1367, 1245, 1100, 841 cm^{-1}. MS: m/e (relative intensity) 170 (M$^+$, 31%), 155 (27), 127 (22), 99 (25), 75 (57), 73 (100). HRMS: Found M$^+$, 170.1130. $C_9H_{18}SiO$ requires M, 170.1127.

2,2-Dimethylcyclopropyl Dimethylphenylsilyl Ketone (1d-p). bp: 85°C (0.3 mmHg). ^{1}H-NMR (400 MHz): δ 0.47 and 0.50 (s, 6H), 0.69 (dd, *J*=7.3, 4.0 Hz, 1H), 0.86 (s, 3H), 1.09 (s, 3H), 1.43 (dd, *J*=5.8, 4.0 Hz, 1H), 2.37 (dd, *J*=7.3, 5.8, Hz, 1H), 7.35~7.61 (m, 5H). ^{13}C-NMR: δ -5.27 and -4.98 (q, $^1J_{CH}$=121 Hz), 18.2 (q,

$^1J_{CH}$=121 Hz), 22.4 (t, $^1J_{CH}$=164 Hz), 27.0 (t, $^1J_{CH}$=126 Hz), 28.8 (s), 41.2 (d, $^1J_{CH}$=160 Hz), 128.0 (d, $^1J_{CH}$=158 Hz), 129.6 (d, $^1J_{CH}$=160 Hz), 133.9 (d, $^1J_{CH}$=159 Hz), 134.7 (s), 243.3 (s). UV: n→π* λmax (ε) 371 (124) nm. IR (neat): 3040, 2960, 1620, 1430, 1380, 840, 820, 780, 740 cm^{-1}. MS: m/e (relative intensity) 232 (M^+, 5%), 217 (17), 189 (46), 161 (30), 35 (100), 75 (21). HRMS: Found M^+, 232.1275. $C_{14}H_{20}SiO$ requires M, 232.1283.

2,2-Dimethylcyclopropyl Dimethyl-t-butylsilyl Ketone (1d-b). bp: 58 °C (0.6 mmHg). ^{1}H-NMR (400 MHz): δ 0.18 and 0.20 (s, 6H), 0.73 (dd, *J*=7.3, 3.7 Hz, 1H), 0.95 (s, 9H), 1.01 (s, 3H), 1.24 (s, 3H), 1.43 (dd, *J*=5.6, 3.7 Hz, 1H), 2.44 (dd, *J*=7.3, 5.6 Hz, 1H). ^{13}C-NMR: δ -7.36 and -7.14 (q, $^1J_{CH}$=120 Hz), 16.9 (s), 18.2 (q, $^1J_{CH}$=126 Hz), 22.8 (t, $^1J_{CH}$=160 Hz), 26.5 (q, $^1J_{CH}$=126 Hz), 27.3 (q, $^1J_{CH}$=126 Hz), 28.7 (s), 41.8 (d, $^1J_{CH}$=159 Hz), 245.0 (s). IR (neat): 2950~2850, 1620, 1460, 1380, 1362, 1255, 1100, 840, 820 cm^{-1}. MS: m/e (relative intensity) 212 (M^+, 3%), 155 (22), 113 (14), 75 (100), 73 (100), 59 (21). HRMS: Found M^+, 212.1581. $C_{12}H_{24}SiO$ requires M, 212.1596.

Phenyl, Benzyl, and Octyl Trimethylsilyl Ketones (1e, 1f, and 1g) were prepared by the reported procedures.[10]

Preparatiom of Salt-Free Dimethyloxosulfonium Methylide (DMSY): DMSY was generated from trimethyloxosulfonium chloride and sodium hydride in THF according to the method of Corey and Chaykowsky.[6a] The resulting NaCl was removed by centrifuge. The stock solution of DMSY was titrated with 0.05N hydrochloric acid just before use.

Salt-Containing DMSY Solution in THF: n-Butyllithium Method : A suspension of trimethyloxosulfonium iodide in THF was treated with 1 equiv. of n-butyllithium in hexane. The resulting soution was allowed to stand at 25°C for 0.5 h before use. **Method by Addition of Salt :** To the salt-free DMSY solution mentioned above was added 1 equiv. of dry lithium iodide or another appropriate inorganic salt.

(Dimethylamino)-*p*-tolyloxosulfonium Methylide (DTSY) was prepared from (dimethylamino)-methyl-*p*-tolyloxosulfonium tetrafluoroborate according to the method of Johnson et al.[11b] The salt-free and salt-containing ylide solutions were prepared in the similar manner mentioned above. **Diphenylsulfonium Methylide (DPSY-M) and Ethylide (DPSY-E)** were prepared by the reaction of diphenylmethyl and diphenylethylsulfonium tetrafluoroborate with n-butyllithium according to the method of Corey.[6a] These ylides were used as salt-containing solution in THF owing to the instability at room temperature.

Thermal Stability of Sulfur Ylides : In a 50 mL round-bottomed flask fitted with a rubber septum, magnetic stirring bar, and an argon inlet was charged 20 mL (5.2×10^{-2} mol/L) of the salt-containing ylide solution prepared above. The solution was sirred at the prescribed temperature. A fraction of the supernatant solution was taken out *via* siringe at regular time intervals and poured into ice-water (10 mL). The resulting aqueous solution was titrated with 0.05 N-HCl. Figure 3 shows relationships between the treatment time and the concentration of the remaining active ylide at the prescribed temperature. The half-life ($\tau^{1/2}$) of each ylide was calculated on the basis on these results.

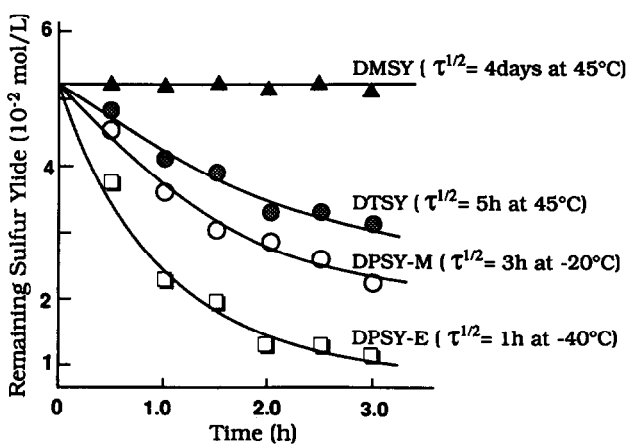


Figure 3. Spontaneous Termal Decomposition of Sulfur Ylides in THF [Half life ($\tau^{1/2}$) of ylide and measurement temp. were indicated in parentheses]

General Procedure for the Reaction of Acylsilanes with DMSY in the Presence of Lithium Iodide (n-Butyllithium method): To a suspension of trimethyloxosulfonium iodide (0.51 mmol) in THF (6 mL) was added *n*-butyllithium (0.51 mmol) *in hexane via* siringe. The resulting ylide mixture was stirred for 0.5 h at 25°C. A THF (4 mL) solution of the desired acylsilane (0.5 mmol) was then added dropwise into the ylide mixture maintained at the prescribed temperature (20°C or -80°C). After being stirred for 2 h, the reaction mixture was diluted with 30 mL of wet pentane at the same temperature, washed with 5 mL of saturated aqueous sodium chloride solution, and dried over anhydrous sodium sulfate. The solvents were removed under reduced pressure to provide the mixture of silyl enol ether (2) and β-ketosilane (3), which were isolated by distillation *in vacuo*. The yield and the product ratio were determined by GC analysis. **(Salt-Free DMSY+LiI Method):** To a suspension of dry lithium iodide (0.5 mmol) in THF was added the salt-free DMSY (0.51 mmol) in THF *via* siringe at 20°C. Then, the THF (4 ml) solution of the desired acylsilane (0.5 mmol) was added dropwise into the ylide mixture maintained at this temperature. After being stirred for 2 h, the reaction mixture was worked up as described above.

General Procedure for the Reaction of Acylsilanes with Salt-Free DMSY. The desired acylsilane (0.5 mmol) in THF was added dropwise into the salt-free DMSY (0.51 mmol) in THF maintained at 20°C. After being stirred for 2 h at this temperature, the reaction mixture was worked up as described above.

The spectral data of 2 and 3 are as follows.

1-(2-n-Butylcyclopropyl)-1-trimethylsiloxyethene (2a). bp: 30°C (0.03 mmHg). ^{1}H-NMR (400 MHz): δ 0.18 (s, 9H), 0.33~0.40 (m, 2H), 0.70~0.75 (m, 1H), 0.89 (t, *J*=7.0 Hz, 3H), 1.09~1.13 (m, 1H), 1.38~1.45 (m, 6H), 3.96 (d, *J*=0.9 Hz, 1H), 4.08 (d, *J*=0.9 Hz, 1H). ^{13}C-NMR: δ 0.12 (q, $^1J_{CH}$=118 Hz), 11.7 (t, $^1J_{CH}$=161 Hz), 14.1 (q, $^1J_{CH}$=125 Hz), 21.3 (d, $^1J_{CH}$=161 Hz), 22.5 (t, $^1J_{CH}$=127 Hz), 23.3 (d, $^1J_{CH}$=159 Hz), 31.6 (t, $^1J_{CH}$=127 Hz), 33.4 (t, $^1J_{CH}$=126 Hz), 87.3 (t, $^1J_{CH}$=158 Hz), 159.3(s). IR (neat): 3100, 2960, 1640, 1255, 1100, 1020, 840 cm^{-1}. Mass: m/e (relative intensity) 212 (M^+,10%), 197 (13), 169 (51), 141 (67), 130 (91), 127 (37), 115 (30), 75 (59), 73 (100). HRMS: Found M^+, 212.1588. $C_{12}H_{24}SiO$ requires M, 212.1596.

1-(2-n-Butylcyclopropyl)-2-Trimethylsilyl-1-ethanone (3a). bp: 57°C (0.03 mmHg). ^{1}H-NMR (400 MHz): δ 0.14 (s, 9H), 0.68 (ddd, *J*=7.9, 5.8, 3.7 Hz, 1H), 0.89 (t, *J*=7.0 Hz, 3H), 1.15~1.20 (m, 1H), 1.22~1.43 (m, 7H), 1.55~1.59 (m, 1H), 2.34 (ABq, *J* =10.4 Hz, 2H). ^{13}C-NMR: δ -1.0 (q, $^1J_{CH}$=120 Hz), 14.0 (q, $^1J_{CH}$=133 Hz), 18.0 (t, $^1J_{CH}$=163 Hz), 22.4 (t, $^1J_{CH}$=120 Hz), 25.4 (d, $^1J_{CH}$=161 Hz), 29.6 (d, $^1J_{CH}$=170 Hz), 31.4 (t, $^1J_{CH}$=121 Hz), 33.0 (t, $^1J_{CH}$=127 Hz), 39.5 (t, $^1J_{CH}$=125 Hz), 208.6 (s). IR (neat): 2950~2850, 1680, 1400, 1340, 1250, 1190, 1120, 1025, 850 cm^{-1}. Mass: m/e (relative intensity) 212 (M^+, 7%), 197 (17), 169 (27), 141 (40), 127 (28), 115 (54), 75 (64), 73 (100). HRMS: Found M^+, 212.1581. $C_{12}H_{24}SiO$ requires M, 212.1596.

1-(2-Phenylcyclopropyl)-1-Trimethylsiloxyethene (2b). bp : 55°C (0.1 mmHg). ^{1}H-NMR: δ -0.11 (s, 9H), 1.0~1.4 (m, 2H), 1.8~2.05 (m, 1H), 2.12~2.27 (m, 1H), 3.92 (d, *J*=1.2 Hz, 1H), 4.07 (d, *J*=1.2 Hz, 1H), 7.28 (seemingly s, 5H). ^{13}C-NMR: δ -0.41 (q, $^1J_{CH}$=119 Hz), 8.8 (t, $^1J_{CH}$=160 Hz), 22.8 (d, $^1J_{CH}$=159 Hz), 24.3 (d, $^1J_{CH}$ =166 Hz), 89.7 (t, $^1J_{CH}$=156 Hz), 125.6 (d, $^1J_{CH}$=159 Hz), 127.6 (d, $^1J_{CH}$=159 Hz), 129.1 (d, $^1J_{CH}$=160 Hz), 138.6 (s), 155.9 (s). IR (neat): 3050~3000, 2960, 1640, 1600, 1500, 1450, 1340, 1260, 1100, 1010, 840 cm^{-1}. Mass: m/e (relative intensity) 232 (M^+, 42%), 218 (85), 141 (93), 117 (65), 115 (63), 104 (100), 91 (49), 77 (24), 75 (100), 73 (99). HRMS: Found M^+, 232.1281. $C_{14}H_{20}SiO$ requires M, 232.1283.

1-(2-Phenylcyclopropyl)-2-Trimethylsilyl-1-ethanone (3b). bp: 61°C (0.15 mmHg). ^{1}HNMR(400 MHz): δ 0.09 (s, 9H), 1.17~1.40 (m, 1H), 1.52~1.84 (m, 1H), 2.01~2.20 (m, 1H), 2.38~2.64 (m, 1H), 2.38 (s, 2H), 7.16~7.23 (m, 5H). ^{13}C-NMR: δ -1.1 (q, $^1J_{CH}$=120 Hz), 12.42 (t, $^1J_{CH}$=162 Hz), 28.6 (d, $^1J_{CH}$=162 Hz), 30.8 (d, $^1J_{CH}$=162 Hz), 40.1 (t, $^1J_{CH}$=124 Hz), 125.8 (d, $^1J_{CH}$=161 Hz), 127.7 (d, $^1J_{CH}$=160 Hz), 129.2 (d, $^1J_{CH}$=161 Hz), 136.1 (s), 204.5 (s). IR (neat): 3000, 2960, 1680, 1604, 1460, 1380, 1258, 1195, 1120, 1060, 1040, 850 cm^{-1}. Mass: m/e (relative intensity) 232 (M^+, 30%), 217 (6), 142 (34), 141 (59), 115 (25), 91(12), 75 (25), 73 (100). HRMS: Found M^+, 232.1275. $C_{14}H_{20}SiO$ requires M, 232.1283.

1-(7-Bicyclo[4.1.0]heptyl)-1-trimethylsiloxyethene (2c). bp: 46°C (0.15 mmHg). ^{1}H-NMR: δ 0.17 (s,

9H), 1.05~1.32 (m, 6H), 1.50~2.02 (m, 5H), 3.92 (d, J=0.7 Hz, 1H), 4.03 (d, J=0.7 Hz, 1H). ^{13}C-NMR: δ 0.12 (q, $^1J_{CH}$=119 Hz), 17.1 (t, $^1J_{CH}$=158 Hz), 21.4 (t, $^1J_{CH}$=126 Hz), 23.0 (t, $^1J_{CH}$=126 Hz), 28.5 (d, $^1J_{CH}$=154 Hz), 86.5 (t, $^1J_{CH}$=157 Hz), 159.5 (s). IR (neat): 3100, 3050, 2950, 2860, 1642, 1450, 1305, 1258, 1040, 1010, 870, 842 cm^{-1}. Mass: m/e (relative intensity) 210 (M^+, 58%), 195 (50), 181 (11), 167 (28), 141 (49), 127 (6), 105 (18), 92 (19), 84 (35), 75 (57), 73 (100). HRMS: Found M^+, 210.1433. $C_{12}H_{22}SiO$ requires M, 210.1440.

1-(7-Bicyclo[4.1.0]heptyl)-2-trimethylsilyl-1-ethanone (3c). bp: 63°C (0.15 mmHg). ^{1}H-NMR (400 MHz): δ 0.13 (s, 9H), 1.14~1.35 (m, 4H), 1.62~1.70 (m, 5H), 1.88~1.95 (m, 2H), 2.32 (s, 2H). ^{13}C-NMR: δ -0.99 (q, $^1J_{CH}$=119 Hz), 21.1 (t, $^1J_{CH}$=125 Hz), 23.0 (t, $^1J_{CH}$=128 Hz), 25.1 (d, $^1J_{CH}$=163 Hz), 35.6 (d, $^1J_{CH}$=162 Hz), 39.7 (t, $^1J_{CH}$=123 Hz), 208.5 (s). IR (neat): 2950~2850, 1670, 1450, 1420, 1310, 1250, 1195, 1110, 1045, 850 cm^{-1}. Mass: m/e (relative intensity) 210 (M^+, 50%), 195 (28), 176 (36), 167 (35), 105 (19), 95 (32), 91 (33), 81 (27), 75 (56), 73 (100). HRMS: Found M^+, 210.1438. $C_{12}H_{22}SiO$ requires M, 210.1440.

1-(2,2-Dimethylcyclopropyl)-1-trimethylsiloxyethene (2d). bp: 60°C (16 mmHg). ^{1}H-NMR (400 MHz): δ 0.21 (s, 9H), 0.53 (d, J=7.3 Hz, 2H), 1.07 (s, 3H), 1.09 (s, 3H), 1.21 (dd, J=7.3, 3.6 Hz, 1H), 4.02 (d, J=0.6 Hz, 1H), 4.10 (d, J=0.6 Hz, 1H). ^{13}C-NMR: δ 0.22 (q, $^1J_{CH}$=120 Hz), 18.1 (s), 18.5 (t, $^1J_{CH}$=158 Hz), 19.4 (q, $^1J_{CH}$=122 Hz), 27.1 (q, $^1J_{CH}$=126 Hz), 30.0 (d, $^1J_{CH}$=150 Hz), 90.2 (t, $^1J_{CH}$=158 Hz), 150.0 (s). IR (neat): 3100, 2950, 1640, 1260, 1220, 1020, 840 cm^{-1}. Mass: m/e (relative intensity) 184 (M^+, 13%), 169 (13), 141 (25), 115 (14), 79 (59), 75 (46), 73 (100), 42 (40). HRMS: Found M^+, 184.1275. $C_{10}H_{20}SiO$ requires M, 184.1283.

1-(2,2-Dimethylcyclopropyl)-2-trimethylsilyl-1-ethanone (3d). bp: 75°C (16 mmHg) . ^{1}H-NMR (400 MHz): δ 0.13 (s, 9H), 0.80 (dd, J=7.6, 3.7 Hz, 1H), 1.15 (s, 3H), 1.18 (s, 3H), 1.20 (dd, J=5.5, 3.7 Hz, 1H), 1.72 (dd, J=7.6, 5.5 Hz, 1H), 2.31 (d, J=10.7 Hz, 1H), 2.37 (d, J=10.7 Hz, 1H). ^{13}C-NMR: δ -1.17 (q, $^1J_{CH}$=119 Hz), 18.0 (q, $^1J_{CH}$=126 Hz), 23.4 (t, $^1J_{CH}$=161 Hz), 26.2 (s), 27.3 (q, $^1J_{CH}$=126 Hz), 35.9 (d, $^1J_{CH}$=159 Hz), 40.8 (t, $^1J_{CH}$=123 Hz), 206.7 (s). IR (neat): 2950, 1680, 1390, 1280, 1195, 1120, 1030, 860 cm^{-1}. Mass: m/e (relative intensity) 184 (M^+, 14%), 169 (11), 141 (27), 115 (14), 79 (58), 75 (46), 73 (100). HRMS: Found M^+, 184.1287. $C_{10}H_{20}SiO$ requires M, 184.1283.

1-(2,2-Dimethylcyclopropyl)-1-dimethylphenylsiloxyethene (2d-p). bp: 76 °C (0.1 mmHg). ^{1}H-NMR: δ 0.38~0.48 (dd, J=7.5, 3.9 Hz, 1H), 0.46 (s, 6H), 1.1 (s, 6H), 1.1~1.3 (m, 2H), 4.0 (d, J=1 Hz, 1H), 4.1 (d, J=1 Hz, 1H), 7.34~7.65 (m, 5H). ^{13}C-NMR: δ -1.0 (q, $^1J_{CH}$=120 Hz), 18.6 (s), 18.6 (t, $^1J_{CH}$=155 Hz), 19.5 (q, $^1J_{CH}$=126 Hz), 27.1 (q, $^1J_{CH}$=126 Hz), 30.0 (d, $^1J_{CH}$=155 Hz), 91.0 (t, $^1J_{CH}$=158 Hz), 127.8 (d, $^1J_{CH}$=163 Hz), 129.6 (d, $^1J_{CH}$=160 Hz), 133.4 (d, $^1J_{CH}$=158 Hz), 137.8 (s), 158.0 (s). IR(neat): 3090, 2960~2850, 1640, 1595, 1430, 1260, 1225, 1120, 1020, 830, 795, 700 cm^{-1}. Mas: m/e 246 (M^+, 18%), 204 (32), 203 (100), 137 (32), 135 (92), 94 (15), 79 (26), 75 (23). HRMS: Found M^+, 246.1432. $C_{15}H_{22}SiO$ requires M, 246.1440.

1-(2,2-Dimethylcyclopropyl)-2-dimethylphenylsilyl-1-ethanone (3d-p). bp: 95°C (0.3 mmHg). ^{1}H-NMR (400 MHz): δ 0.38 and 0.41 (s, 6H), 0.71 (dd, J=7.6, 4.0 Hz, 1H), 1.00 (s, 3H), 1.07 (s, 3H), 1.15 (dd, J=5.5, 4.0 Hz, 1H), 1.60 (dd, J=7.6, 5.5 Hz, 1H), 2.54 (ABq, J=10.7 Hz, 2H), 7.36~7.60 (m, 5H). ^{13}C-NMR: δ -2.7 and -2.3 (each q, $^1J_{CH}$=129 Hz), 17.9 (q, $^1J_{CH}$=124 Hz), 23.9 (t, $^1J_{CH}$=160 Hz), 26.7 (s), 27.2 (q, $^1J_{CH}$=127 Hz), 36.3 (d, $^1J_{CH}$=160 Hz), 40.0 (t, $^1J_{CH}$=122 Hz), 127.9 (d, $^1J_{CH}$=156 Hz), 129.4 (d, $^1J_{CH}$=160 Hz), 133.5 (d, $^1J_{CH}$=158 Hz), 137.3 (s), 206.8 (s). IR(neat) : 3050, 2950, 1680, 1595, 1430, 1390, 1260, 1200, 1120, 1024, 840 (broad), 740, 700 cm^{-1}. Mass: m/e 246 (M^+, 6%), 231 (4), 204 (7), 203 (42), 168 (13), 137 (25), 135 (100), 94 (5), 79 (20), 75 (18). HRMS: Found M^+, 246.1438. $C_{15}H_{22}SiO$ requires M, 246.1440.

1-(2,2-Dimethylcyclopropyl)-1-t-butyldimethylsiloxyethene (2d-b). ^{1}H-NMR: δ 0.16 and 0.17 (s, 6H), 0.51~0.56 (m, 2H), 0.93 (s, 9H), 1.07 (s, 3H), 1.08 (s, 3H), 1.23 (dd, J=7.3, 6.4 Hz, 1H), 4.00 (seemingly d, 1H), 4.11 (seemingly d, 1H). ^{13}C-NMR: δ -4.6 and -4.5 (q, $^1J_{CH}$=120 Hz), 18.2 (s), 18.5 (t, $^1J_{CH}$=156 Hz), 19.5 (q, $^1J_{CH}$=126 Hz), 25.8 (q, $^1J_{CH}$=125 Hz), 27.2 (q, $^1J_{CH}$=126 Hz), 30.2 (d, $^1J_{CH}$=156 Hz), 90.1 (t, $^1J_{CH}$=157 Hz), 158.3 (s). IR (neat): 2960~2850, 1635, 1260, 1230, 1120, 1020, 830 cm^{-1}. Mass: m/e (relative intensity) 226 (M^+, 3%), 183 (9), 169 (24), 127 (74), 79 (11), 75 (100). HRMS: Found M^+, 226.1759. $C_{13}H_{26}SiO$ requires M, 226.1753.

1-(2,2-Dimethylcyclopropyl)-2-t-butyldimethylsilyl-1-ethanone (3d-b). ^{1}H-NMR: δ 0.07 and 0.10 (s, 6H), 0.81 (dd, *J*= 7.6, 3.9 Hz, 1H), 0.91 (s, 9H), 1.16 (s, 3H), 1.18 (s, 3H), 1.19 (dd, *J*= 5.5, 3.9 Hz, 1H), 1.73 (dd, *J*=7.6, 5.5Hz, 1H), 2.32 (s, 2H). IR (neat): 2950, 1675, 1395, 1260, 1200, 1120, 1020, 860~820 (broad) cm^{-1}. Mass: m/e (relative intensity) 226 (M^+, 2%), 170 (34), 169 (100), 170 (34), 127 (25), 111 (32), 75 (100), 73 (71), 59 (9). HRMS: Found M^+, 226.1742. $C_{13}H_{26}SiO$ requires M, 226.1753.

1-Phenyl-1-trimethylsiloxyethene (2e). bp : 46°C (0.2 mmHg). ^{1}H-NMR: δ 0.27 (s, 9H), 4.42 (d, *J*=1.7 Hz, 1H), 4.91 (d, *J*=1.7 Hz, 1H), 7.22~7.62 (m, 5H), in agreement with literature value.[4a]

1-Phenyl-2-trimethylsilyl-1-ethanone (3e). bp: 55~60 °C (0.2 mmHg). ^{1}H-NMR : δ 0.08 (s , 9H), 2.72 (s, 2H), 7.8~8.0 (m, 5H), in agreement with literature value.[4a]

3-Phenyl-2-trimethylsiloxy-1-propene (2f). bp: 42°C (0.4 mmHg). ^{1}H-NMR: δ 0.10 (s ,9H), 3.30 (s, 2H), 4.06 (d, *J*=0.7 Hz, 1H), 4.11 (d, *J*=0.7 Hz, 1H), 7.22 (seemingly s, 5H). IR (neat): 3100~3000, 2950~2850, 1650, 1620, 1595, 1450, 1120, 1020, 740 cm^{-1}. HRMS: Found M^+, 206.1132. $C_{12}H_{18}SiO$ requires M, 206.1127.

1-Phenyl-3-trimethylsilyl-2-propanone (3f). bp: 82 °C (0.4 mmHg). ^{1}H-NMR: δ 0.13 (s, 9H), 2.26 (s, 2H), 3.63 (s, 2H), 7.15~7.36 (m, 5H). IR (neat): 3100~3000, 2950~2850, 1695, 1600, 1500, 1410, 1260, 850 (broad), 740 cm^{-1}. HRMS: Found M^+, 206.1134. $C_{12}H_{18}SiO$ requires M, 206.1127.

Reaction of Acylsilanes with DTSY or DPSY. To a suspension of diphenylmethyl or diphenylethyl tetrafluoroborate (0.5 mmol) in THF (6 mL) cooled to -80°C was added *n*-butyllithium (0.51 mmol) in hexane *via* siringe. The resulting ylide mixture was allowed to stir for 15 min at this temperature. The desired acylsilane (0.5 mmol) in THF (4 mL) was then added dropwise into this ylide mixture. After being stirred for 2 h at this temperature, the reaction mixture was worked up as mentioned above. Separation of β-ketosilanes (3) and epoxysilanes (5) produced was carried out by a flash column chromatography (silica gel, hexane/benzene, 1:1, as eluent). During this operation, sigificant amonunts of 3 were converted to the corresponding methyl or ethyl ketones by the protiodesilylation. Analytical sample of 3 was obtained by the bulb-to-bulb distillation of the mixture of 3 and the methyl or ethyl ketones. The yield and the product ratio were determined by GC analysis of the crude product.

The spectral data of 3 and 5 are as follows.

1-(7-Bicyclo[4.1.0]heptyl)-2-trimethylsilyl-1-propanone (3c-m). ^{1}H-NMR: δ 0.09 (s , 9H), 1.1~1.4 (m, 4H), 1.15 (d, *J*=6.8 Hz, 3H), 1.5~2.0 (m, 6H), 2.59 (q, *J*= 6.8 Hz, 2H). IR (neat): 2950~2850, 1680, 1450, 1415, 1320, 1250, 1150, 840 (broad) cm^{-1}. HRMS: Found M^+, 224.1599. $C_{13}H_{24}SiO$ requires M, 224.1596.

1-(2,2-Dimethylcyclopropyl)-2-trimethylsilyl-1-propanone (3d-m). ^{1}H-NMR: δ 0.10 (s, 9H), 0.70 (dd, *J*=7.6, 3.8 Hz, 1H), 1.16 (d, *J*=6.8 Hz, 3H), 1.16 (s, 3H), 1.18 (s, 3H), 1.17~1.21 (m, 1H), 1.70 (dd, *J*=7.6, 5.6 Hz, 1H), 2.58 (q, *J*=6.8 Hz, 1H). IR (neat): 2950~2850, 1690, 1450, 1270, 860 (broad) cm^{-1}. HRMS: Found M^+, 198.1421. $C_{11}H_{22}SiO$ requires M, 198.1439.

1-Phenyl-2-trimethylsilyl-1-propanone (3e-m). ^{1}H-NMR: δ -0.04 (s, 9H), 1.33 (d, *J*=7.0 Hz, 3H), 3.38 (q, *J*=7.0 Hz, 1H), 7.3~7.6 (m, 5H). IR (neat): 3100~3000, 2950~2850, 1695, 1595, 1430, 840 (broad) cm^{-1}. HRMS: Found M^+, 206.1124. $C_{12}H_{18}SiO$ requires M, 206.1127.

1-Phenyl-3-trimethylsilyl-2-butanone (3f-m). bp: 82 °C (0.4 mmHg). ^{1}H-NMR: δ 0.12 (s , 9H), 1.14 (d, *J*=6.8 Hz, 3H), 2.56 (q, *J*=6.8 Hz, 1H), 3.64 (s, 2H), 7.0~7.5 (m, 5H). IR (neat): 3100~3000, 2950~2850, 1690, 1600, 1450, 1330, 840 (broad), 700 cm^{-1}. HRMS: Found M^+, 220.1265. $C_{13}H_{20}SiO$ requires M, 220.1283.

1-Trimethylsilyl-2-decanone (3g). ^{1}H-NMR: δ 0.12 (s, 9H), 0.88 (t, *J*=7.3 Hz, 3H), 1.26 (broad s, 10H), 1.4~1.6 (m, 2H), 2.21 (s, 2H), 2.34 (t, *J*=7.3Hz, 2H). IR (neat): 3000~2850, 1695, 1460(broad), 1410, 1255, 1190, 1130, 840 (broad), 700 cm^1. HRMS: Found M^+, 228.1914. $C_{13}H_{28}SiO$ requires M, 228.1909.

2-Trimethylsilyl-3-undecanone (3g-m). ^{1}H-NMR: δ 0.1 (s, 9H), 0.87 (t, *J*=7.3 Hz, 3H), 1.15 (d, *J*=6.8 Hz, 3H), 1.3 (broad s, 10H), 1.4~1.6 (m, 2H), 2.25 (t, *J*=7.3 Hz, 2H), 2.35 (q, *J*=6.8 Hz, 1H). IR (neat): 3000~2850, 1690, 1460, 1260, 1150, 840 (broad) cm^1. HRMS: Found M^+, 224.2059. $C_{14}H_{30}SiO$ requires M, 224.2066.

3-Phenyl-2-Trimethylsilyl-1,2-epoxypropane (5f). ^{1}H-NMR: δ 0.14 (s, 9H), 2.28 (s, 2H), 3.64 (s, 2H),

7.12~7.36 (m, 5H). IR: 3100~3000, 3000~2850, 1600, 1480, 1250, 840 (broad), 760 cm^{-1}. HRMS: Found M^+, 206.1135. $C_{12}H_{18}SiO$ requires M, 206.1127.

1-Phenyl-2-trimethylsilyl-2,3-epoxybutane (5f-m). ^{1}H-NMR: δ -0.19 (s, 9H), 1.49 (d, *J*=5.6 Hz, 3H), 3.07 (q, *J*=5.4 Hz, 1H), 2.91 (ABq, *J*=15.4 Hz, 2H), 7.25 (s, 5H). IR (neat): 3100~3000, 3000~2850, 1605, 1500, 1460, 1410, 1250, 840 (broad), 760, 700 cm^{-1}. HRMS: Found M^+, 220.1278. $C_{13}H_{20}SiO$ requires M, 220.1283.

2-Trimethylsilyl-1,2-epoxydecane (5g). ^{1}H-NMR: δ 0.06 (s, 9H), 0.88 (t, *J*=7.0 Hz, 3H), 1.25 (broad s, 12H), 1.4~1.6(m, 2H), 2.60 (s, 2H) . IR (neat): 3000~2850, 1460(broad), 1250, 840 (broad), 750, 660 cm^{-1}. HRMS: Found M^+, 228.1928. $C_{13}H_{28}SiO$ requires M, 228.1909.

3-Trimethylsilyl-2,3-epoxyundecane (5g-m). ^{1}H-NMR: δ 0.05 (s, 9H), 0.88 (t, *J*=7.3 Hz, 3H), 1.27 (broad s, 12H), 1.32 (d, *J*=5.4 Hz, 3H), 1.4~1.6 (m, 2H), 2.91 (q, *J*=5.4 Hz, 1H). IR (neat): 3000~2850, 1470, 1410, 1260, 850 (broad), 760 cm^{-1}. HRMS: Found M^+, 242.2101. $C_{14}H_{30}SiO$ requires M, 242.2066.

Treatment of the Mixture of Siloxyalkene (2) and β-Ketosilane (3) with DMSY. In a 10 ml round-bottomed flask fitted with a rubber septum, mechanical stirrer, and argon inlet was charged a mixture of **2d** (0.074 mmol) and **3d** (0.09 mmol) in THF (3 ml). The salt-containing DMSY(0.08 mmol) solution prepared by the butyllithium method was added to the above mixture at 0°C, and stirred at 25°C. A fraction of the solution was taken out *via* siringe at regular time intervals and quenched with wet pentane. The resulting mixture was analyzed by GC. The results were summarized in Figure 1.

Treatment of the Mixture of β-Ketosilane (3) and Epoxysilane (5) with DMSY. A mixture of **3g-m** (0.14 mmol) and **5g-m** (0.09 mmol) in THF (5 mL) was treated with the salt-containing DMSY (0.11 mmol) solution in the similar manner described above. A fraction of the solution was taken out *via* siringe at regular time intervals and quenched with wet pentane. The resulting mixture was analyzed by GC. The results were shown in Figure 2.

Cross-Over Experiments: A mixture of **1a** (0.25 mmol) and **1d-p** (0.25 mmol) in THF (4 mL) was treated with the DMSY (0.52 mmol) solution prepared by using n-butyllithium according to the general procedure described above. The reaction mixture was worked up as mentioned above. GC analysis of the reaction mixture at 20°C showed the formation of **2a**, **2d-p**, **3a**, and **3d-p** in the ratio of 6 : 18 : 41 : 35. At -80°C, **2a**, **2d-p**, **3a**, and **3d-p** were formed in the ratio of 22 : 53 : 21 : 4.

Solubility of Salts in Salt-Free DMSY Solution was determined by measuring the amount of salt dissolved in DMSY solution, which was weighed as the corresponding sulfate; In a 50 mL centrifuge tube containing a stirring bar and fitted with a rubber septum was placed an 40 mmol of dry inorganic salt (LiI, NaI, KI, or $LiBF_4$) under an argon atmosphere. A 10 mL of the salt-free DMSY (0.323 mol/L) in THF, ether, or dioxane was added to the system *via* syringe. The mixture was stirred about 10 min at 20°C and then centrifuged. A 5 mL of the supernatant solution was taken out and poured into 10 mL of water to decompose DMSY. To this aqueous solution was added 2~3 drops of concentrated sulfuric acid. The resulting mixture was concentrated carefully on water-bath, transferred to a weighing dish, evaporated to dryness, ignited at 600°C, and weighed as the corresponding sulfate. The results were shown in Table 3.

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