Conversion of Carbon–Sulfur Linkages into Carbon–Silicon Ones *via* Reductive Silylation. Preparation of Silyl Enol Ethers of Acyltrimethylsilanes[1)]

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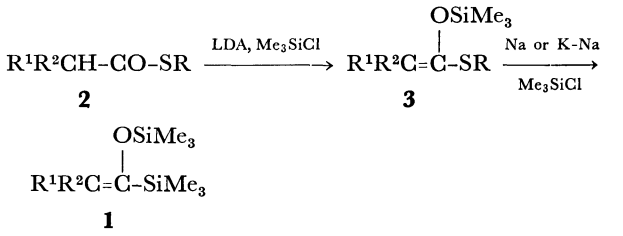
Reductive cleavage of carbon–sulfur linkages of silyl enol ethers of thiocarboxylic *S*-esters can be induced by treatment with sodium or potassium–sodium alloy in the presence of chlorotrimethylsilane, and the corresponding silyl enol ethers of acyltrimethylsilanes can be prepared in high yields.

Various organosilicon compounds have recently been employed as useful intermediates in a wide range of synthetic organic chemistry.[2)] Acyltrimethylsilanes were initially prepared from an interest of their unique spectral properties. However, it has recently been found that they have interesting properties as synthetic intermediates.[3)] Compounds of this type are usually prepared by silylation of various acyl anion equivalents,[4)] appropriate 1-trialkylsilyl-1-alkanol derivatives also being employed for their preparation.[5,6)] This paper describes a new approach to the generation of acyl anion equivalents from silyl enol ethers of thiocarboxylic *S*-esters, by which acyltrimethylsilanes can be prepared as their silylated enols.

Reductive silylation of unsaturated organic compounds[7)] with alkali metal, *e.g.* sodium or potassium–sodium alloy, has been found to be a most useful method for the synthesis of organosilicon compounds.[8)] Carbon–sulfur linkages undergo cleavage with metallic lithium in the presence of an appropriate proton source. Such a procedure has frequently been employed for removal of sulfur group from various sulfides.[9)] It was thus expected that treatment of sulfides with alkali metal and chlorotrimethylsilane would make it possible to convert the carbon–sulfur linkages into the corresponding carbon–silicon ones through silylation of the initially generated carbanionic species. Such a transformation has recently been reported by using alkyl phenyl sulfides.[10,11)]

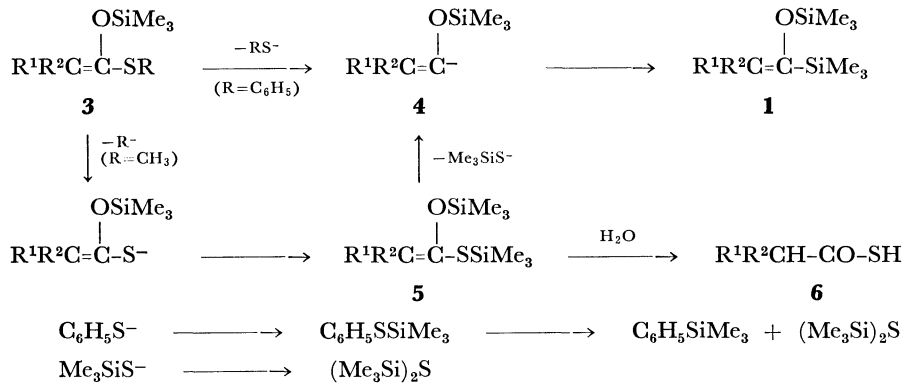
Studies were carried out on the application of this procedure to the synthesis of silyl enol ethers of acyltrimethylsilanes **1**, used also for the preparation of parent acyltrimethylsilanes and their α-functionalized derivatives.[12)] Silyl enol ethers **3** of thiocarboxylic *S*-esters were prepared by treating the corresponding esters **2** with lithium diisopropylamide (LDA) and then with chlorosilane.[13)] Of the esters examined, succinic and glutaric esters gave no silyl enol ethers because of a facile intramolecular cyclization reaction of the ester enolate anion generated initially. Except for the above cases, various *S*-methyl and *S*-phenyl esters gave the desired silylated enols **3** in excellent yields.

A preliminary study on the effect of substituent on thiocarboxylic acid in the reductive silylation has been carried out by using the silylated enols of *S*-methyl, *S*-ethyl, and *S*-phenyl 3-phenylpropanethioates **3**. From the results, enols of *S*-methyl ester **3** ($R^1=C_6H_5CH_2$, $R^2=H$, $R=CH_3$) and of *S*-phenyl ester **3** ($R^1=C_6H_5CH_2$, $R^2=H$, $R=C_6H_5$) were found to undergo the expected reductive silylation to afford the corresponding silyl enol ether **1** ($R^1=C_6H_5CH_2$, $R^2=H$) in good yields, while that of *S*-ethyl ester **3** ($R^1=C_6H_5CH_2$, $R^2=H$, $R=C_2H_5$) was almost inert under similar reaction conditions. In the reaction with *S*-phenyl ester derivative, (phenylthio)trimethylsilane was also formed as one of the side-products, which decreased through its conversion into phenyltrimethylsilane on prolonged reaction period. On the effect of the substituent on sulfur atom in reactions of this type, the following unique features of methyl and phenyl groups have been observed. (1) In the reductive silylation of sulfides, alkyl phenyl sulfides usually undergo a facile bond cleavage between alkyl and sulfur to give alkyltrimethylsianes together with (phenylthio)trimethylsilane, but not dialkyl sulfides.[10)] (2) In the reaction with disulfides, dialkyl and diphenyl disulfides afford the corresponding thiosilanes, but dimethyl disulfide gives bis(trimethylsilyl) sulfide exclusively.[11)]

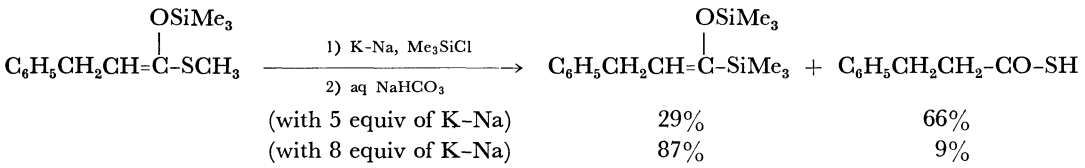


Scheme 1.

The results indicate that the phenylthio group might enhance the cleavage of another bond with sulfur of **3**, giving the corresponding carbanionic species **4** directly. On the other hand, in the reactions with the *S*-methyl ester derivative, the linkage between sulfur and methyl seems to be cleaved preferentially to the bond of sulfur with the vinyl group of **3**. 1-Trimethylsiloxy-1-trimethylsilylthio-1-alkene **5** appears to be generated as an initial intermediate and then converted into the silylated enol **1** through the bond scission between sulfur and the vinyl group. This was confirmed by the following controll experiments. Treatment of **3** ($R^1=C_6H_5CH_2$, $R^2=H$, $R=CH_3$) with 5 equiv of potassium–sodium alloy in the presence of chlorotrimethylsilane, followed by aqueous work-up of the reaction mixture gave rise to the formation of the corresponding thiocarboxylic acid **6** as a major product (66%) together with **1** ($R^1=C_6H_5CH_2$, $R^2=H$) (29%), while the reaction with 8 equiv of the same reducing agent afforded **1** ($R^1=C_6H_5CH_2$, $R^2=$



Scheme 2.



(1)

Table 1. Preparation of trimethylsilyl enol ethers of thiocarboxylic *S*-esters **3**

R^1	R^2	R	Yield (%)	Bp (°C/mmHg)[a]	Anal. (*m/e*)
CH_3	H	CH_3	83	110—112/102	Found: 176.0680. Calcd for $C_7H_{16}OSSi$: M, 176.0691.
CH_3	CH_3	CH_3	86	102—103/55	Found: 190.0822. Calcd for $C_8H_{18}OSSi$: M, 190.0848.
C_4H_9	H	CH_3	91	128—130/33	Found: 218.1143. Calcd for $C_{10}H_{22}OSSi$: M, 218.1161.
C_4H_9	H	C_6H_5	95	104—105/0.5	Found: 280.1333. Calcd for $C_{15}H_{24}OSSi$: M, 280.1317.
C_6H_{13}	H	C_6H_5	96	109—112/0.1	Found: 308.1609. Calcd for $C_{17}H_{28}OSSi$: M, 308.1630.
C_8H_{17}	H	C_6H_5	96	152—154/0.75	Found: 336.1928. Calcd for $C_{19}H_{32}OSSi$: M, 336.1943.
$C_6H_5CH_2$	H	CH_3	93	115—116/6	Found: 252.0988. Calcd for $C_{13}H_{20}OSSi$: M, 252.1004.
$C_6H_5CH_2$	H	C_6H_5	92	123—125/0.13	Found: 314.1140. Calcd for $C_{18}H_{22}OSSi$: M, 314.1161.
$CH_2=CH(CH_2)_7$-	H	C_6H_5	92	135—138/0.15	Found: 348.1931. Calcd for $C_{20}H_{32}OSSi$: M, 348.1943.
-$(CH_2)_5$-		C_6H_5	92	90—91/0.08	Found: 292.1331. Calcd for $C_{16}H_{24}OSSi$: M, 292.1317.
C_2H_5O	H	CH_3	85	110—112/35	Found: 206.0782. Calcd for $C_8H_{18}O_2SSi$: M, 206.0797.
$CH_3C(C_2H_4O_2)CH_2$	H	C_6H_5	91	123—125/10	Found: 324.1231. Calcd for $C_{16}H_{24}O_3SSi$: M, 324.1215.
CH_3S	H	CH_3	90	97—99/10	Found: 208.0430. Calcd for $C_7H_{16}OS_2Si$: M, 208.0412.
C_2H_5S	H	CH_3	92	128—130/23	Found: 222.0552. Calcd for $C_8H_{18}OS_2Si$: M, 222.0568.

a) 1 mmHg = 133.322 Pa.

H) in 87% yield accompanied by thiocarboxylic acid **6** (9%) under similar reaction conditions.

The phenylthio and trimethylsilylthio groups seem to make the cleavage of the bond between sulfur and 1-(trimethylsiloxy)vinyl group feasible, but neither ethylthio and its homologs.

Excess amount of the reducing agent should be used in order to achieve the transformation. Otherwise, the starting material is recovered in the reaction with *S*-phenyl ester derivative **3** (R=C_6H_5), or the corresponding thiocarboxylic acid is obtained in the case with *S*-methyl ester derivative **3** (R=CH_3) in a large amount, although theoretically required amounts should be 4 equiv of the reducing agent to 1 equiv of **3** even if the reaction proceeds through an initial removal of R groups of **3**. This is a great difference from acyloin condensation, which usually proceeds with almost stoichiometric amount of the reducing agent.[7a] We have used 8—9 equiv of sodium dispersion or potassium–sodium alloy to achieve an efficient conversion into **1**.

With sodium dispersion prepared by heating in tolune or xylene, the results are sometimes irreproducible probably because of the difference in the grade of dispersion of the reducing agent. Use of commercial sodium dispersion[14] could eliminate such difficulties to give the desired silylated enol **1** over 80% yields. The usual potassium–sodium alloy can advatageously be used, especially for large scale preparation, to give slightly higher yields in comparison with the commercial sodium dispersion.

As a solvent, benzene is preferable to tetrahydrofuran or ether. Some unidentified products are formed in noticeable amount when tetrahydrofuran is used.

When start from *S*-phenyl ester derivative **3**, (phenylthio)trimethylsilane and phenyltrimethylsilane were also formed as by-products, sometimes making it difficult to separate the desired silyl enol ether **1** by distillation.

In such a case, *S*-methyl ester derivative **3** (R=CH_3) would be preferable since the side-product, bis(trimethylsilyl) sulfide, can be removed by a simple hydrolytic work-up of the reaction mixture. A small amount of 1-trimethylsiloxy-1-trimethylsilylthio-1-alkene **5** sometimes still remains in the reaction mixture, but it can be removed by treatment with aq $NaHCO_3$ solution. GLPC and NMR analyses of the resulting crude mixtures show that they are pure enough for further synthetic use without purification. For example, acidic hydrolysis[5a,e] or treatment with chlorine [12a] affords the corresponding acyltrimethylsilane or its α-chlorinated derivative almost quantitatively.

Some functional groups are compatible with the present procedure (Table 2), no difficulty being encountered in the reductive silylation of the *S*-phenyl or *S*-methyl ester derivative **3** having olefinic or acetal group.

With the α-alkoxy derivative of **3**, a side reaction such as β-elimination of the intermediate **4** into the corresponding acetylenic ether might be expected. However, from a starting material such as **3** (R^1=

TABLE 2. PREPARATION OF 1-TRIMETHYLSILYL-1-TRIMETHYLSILOXY-1-ALKENES **1**[a]

R^1	R^2	Bp(°C/mmHg)[b]	Yield(%)	IR(neat) cm^{-1}; NMR[c](CCl$_4$) δ; Elemental analyses %
CH_3	H	100—104/100	74[d]	1620, 1250, 1150, 850; 0.06(s, 9H), 0.13(s, 9H), 1.58(d, J=7 Hz, C$\underline{H}_3$CH=C), 1.63(d, J=7 Hz, C$\underline{H}_3$CH=C), 5.05 (q, J=7 Hz, $CH_3C\underline{H}$=C), 5.43(q, J=7 Hz, $CH_3C\underline{H}$=C); Found: C, 53.22; H, 10.81. Calcd for $C_9H_{22}OSi_2$: C, 53.40; H, 10.95.
CH_3	CH_3	82—83/18	81[d]	1610, 1250, 1125, 840; 0.20(s, 9H), 0.28(s, 9H), 1.65(s, 3H), 1.77(s, 3H); Found: C, 55.63; H, 11.02. Calcd for $C_{10}H_{24}OSi_2$: C, 55.47; H, 11.18.
C_4H_9	H	70—72/7	87[d] 87[e]	1605, 1250, 1115, 840; 0.10(s, 9H), 0.13(s, 9H), 0.70—1.50(m, 7H), 1.75—2.25(m, 2H), 4.85(t, J=7 Hz, $CH_2C\underline{H}$=C), 5.28(t, J=7 Hz, $CH_2C\underline{H}$=C); Found: C, 59.21; H, 11.77. Calcd for $C_{12}H_{28}OSi_2$: C, 58.94; H, 11.54.
C_6H_{13}	H	119—120/12	82[e]	1607, 1250, 1110, 840; 0.13(s, $\underline{Me}_3$Si), 0.23(s, $\underline{Me}_3$Si), 1.00 (t, J=3 Hz, 3H), 1.38(s, 8H), 1.80—2.33(m, 2H), 5.03(t, J=6 Hz, 1H); Found: C, 61.74; H, 11.79. Calcd for $C_{14}H_{32}OSi_2$: C, 61.69; H, 11.61.
C_8H_{17}	H	93—95/0.7	94[e]	1610, 1250, 1100, 850; 0.17(s, 9H), 0.26(s, 9H), 1.00(t, J=4 Hz, 3H), 1.32—1.71(m, 12H), 1.86—2.47(m, 2H), 5.02(t, J=7 Hz, 1H); Found: C, 64.09; H, 12.29. Calcd for $C_{16}H_{36}OSi_2$: C, 63.92; H, 12.07.
$C_6H_5CH_2$	H	90—92/0.25	87[d] 84[d,f] 82[e]	1590, 1245, 1115, 840; 0.15(s, 9H), 0.18(s, 9H), 3.27(d, J=8 Hz, C$\underline{H}_2$CH=C), 3.40(d, J=6.5 Hz, C$\underline{H}_2$CH=C), 5.10 (t, J=6.5 Hz, $CH_2C\underline{H}$=C), 5.48(t, J=8 Hz, $CH_2C\underline{H}$=C), 7.08(s, 5H); Found: C, 64.80; H, 9.34. Calcd for $C_{15}H_{26}OSi_2$: C, 64.68; H, 9.41.
CH_2=CH$(CH_2)_7$	H	135—138/0.15	88[e]	1639, 1609, 1250, 1110, 850; 0.20(s, 18H), 1.39(s, 10H), 1.89—2.27(m, 4H), 4.87—5.23(m, 2H), 5.55—5.97 (m, 2H); Found: C, 65.28; H, 11.63. Calcd for $C_{17}H_{36}OSi_2$: C, 65.31; H, 11.61.
$-(CH_2)_5-$		100—102/10	88[e]	1610, 1250, 1120, 850; 0.16(s, 18H), 1.17—1.86(m, 6H), 2.00—2.50(m, 4H); Found: C, 61.03; H, 11.23. Calcd for $C_{13}H_{28}OSi_2$: C, 60.87; H, 11.00.
C_2H_5O	H	80—82/28	70[d]	1626, 1245, 1150, 1110, 845; 0.18(s, 18H), 1.07(t, J=7 Hz, C$\underline{H}_3$CH$_2$O), 1.12(t, J=7 Hz, C$\underline{H}_3$CH$_2$O), 3.45(q, J=7 Hz, $CH_3C\underline{H}_2O$), 3.55(q, J=7 Hz, $CH_3C\underline{H}_2O$), 5.27(s, C$\underline{H}$=C), 6.20(s, C$\underline{H}$=C); Found: C, 51.80; H, 10.53. Calcd for $C_{10}H_{24}O_2Si_2$: C, 51.65; H, 10.41.
$CH_3C(C_2H_4O_2)CH_2$	H	87—89/1.5	82[d]	1600, 1245, 840; 0.05(s, 9H), 0.13(s, 9H), 1.17(s, 3H), 2.22(d, J=7 Hz, C$\underline{H}_2$CH=C), 2.27(d, J=7 Hz, C$\underline{H}_2$CH=C), 3.72(s, 4H), 4.98(t, J=7 Hz, $CH_2C\underline{H}$=C); Found: C, 54.32; H, 9.95. Calcd for $C_{13}H_{28}O_3Si_2$: C, 54.12; H, 9.78.

a) All reactions were carried out in 10 mmol scale unless otherwise stated. b) 1 mmHg=133.322 Pa. c) Values obtained by using benzene or dichloromethane as an internal standard. d) Reactions carried out with the *S*-methyl ester derivative **3** by using potassium-sodium alloy. e) Reactions carried out with the *S*-phenyl ester derivative **3** by using commercial sodium dispersion. f) Reaction carried out in 0.1 mol scale.

OC_2H_5, R^2=H, R=CH_3), the corresponding silyl enol ether **1** (R^1=OC_2H_5, R^2=H) could be obtained satisfactorily, the yield decreasing slightly.

In contrast, with the α-alkylthio or α-phenylthio derivative **3**, β-elimination seems to take place from the intermediate **4** predominantly, no corresponding product being isolated. The solution usually turns dark purple during the course of reductive silylation, but in these cases such kind of color change has never been observed.

In contrast to the inert behavior of dialkyl sulfides to the present reducing system, various thioacetals appear to undergo a facile bond cleavage between carbon and sulfur, and the reaction with *S*-methyl ester derivative **3** having diethyl thioacetal or ethylene thioacetal group resulted in the formation of complex mixtures.

Experimental

All boiling points are uncorrected. IR spectra were recorded on a Hitachi 260-10 spectrometer, and NMR spectra on a Hitachi R-24B spectrometer using dichloromethane or benzene as an internal standard.

Materials. Tetrahydrofuran (THF) and benzene were purified shortly before use by drying and distillation over sodium-benzophenone or sodium. Chlorotrimethylsilane was purified by distillation over sodium wire. Thiocarboxylic *S*-phenyl esters were prepared by treating the corresponding acyl chlorides with benzenethiol in the presence of triethylamine in ether. *S*-Methyl esters were prepared by treating dichloromethane solution of the corresponding acyl chlorides with aqueous solution of sodium methanethiolate in the presence of tetrabutylammonium bromide.

Preparation of Trimethylsilyl Enol Ethers of Thiocarboxylic S-Esters **3**. *General Procedure*: Lithium diisopropylamide (LDA) was prepared by treating diisopropylamine (2.47 g, 24.5 mmol) and butyllithium (14.9 ml of 1.64 molar hexane solution, 24.5 mmol) in tetrahydrofuran at −78 °C under argon atmosphere. An appropriate thiocarboxylic *S*-ester (20 mmol) in tetrahydrofuran (10 ml) was added over a period of 10 min to the resulting LDA solution at −78 °C. After further addition of chlorotrimethylsilane (3.26 g, 30 mmol) for 1 min, the resulting mixture was warmed up to room temperature and stirred at that temperature for 2h. The solvent was then removed *in vacuo* and the remaining residue diluted with hexane (20 ml). The salt deposited was filtered off by means of a hyflo super cell. Removal of the solvent from the filtrate followed by fractional distillation afforded the corresponding silyl enol ether **3**. Elementary compositions of the products were determined by means of high mass spectra with use of a Hitachi RMU-7M mass spectrometer. The results are given in Table 1.

Preparation of Trimethylsilyl Enol Ethers of Acyltrimethylsilanes. ***1*** *(A) Reductive Silylation of* ***3*** *with Sodium Dispersion and Chlorotrimethylsilane*: Sodium dispersion[14] (3.68 g of 50% paraffin contained, 0.08 g atom) was washed three times with hexane (10 ml) and once with benzene (10 ml). It was then mixed with benzene (35 ml) and introduced into a flask filled with argon with a hypodermic syringe. Chlorotrimethylsilane (8.68 g, 80 mmol) was then added. To the resulting solution was added a benzene (15 ml) solution of an appropriate silyl enol ether **3** (10 mmol) during the course of 10 min. After addition was complete, the reaction mixture was heated to refluxing for 2 h. The reaction mixture was filtered through the hyflo super cell and the filtrate concentrated *in vacuo*. The residual oil was washed with 1:1 aqueous tetrahydrofuran (10 ml) solution of satd sodium hydrogencarbonate, and extracted with hexane (20 ml). After drying over anhydrous Mg_2SO_4, removal of the solvent followed by fractional distillation gave the trimethylsilyl enol ether of the corresponding acyltrimethylsilane **1**. The results are given in Table 2.

Preparation of Trimethylsilyl Enol Ethers of Acyltrimethylsilanes ***1***. *(B) Reductive Silylation of* ***3*** *with Potassium–Sodium Alloy and Chlorotrimethylsilane*: The alloy was prepared by heating a mixture of metallic potassium (1.56 g, 0.04 g atom) and sodium (0.92 g, 0.04 g atom) in a flask filled with argon To this was added a benzene (35 ml) solution of chlorotrimethylsilane (8.68 g, 80 mmol). To the resulting solution was added an appropriate trimethylsilyl enol ether of thiocarboxylic *S*-ester **3** (10 mmol) in benzene (15 ml) at room temperature over a period of 10 min. Gentle refluxing took place immediately. After addition was complete, the reaction mixture was stirred at room temperature for 4.5 h. The reaction mixture was then treated in a similar way to that described above, the trimethylsilyl enol ether of the corresponding acyltrimethylsilane **1** being obtained (Table 2).

Controll Experiment. The reaction was carried out with the silyl enol ether of *S*-methyl 3-phenylpropanethioate **3** (R^1=$C_6H_5CH_2$, R^2=H, R=CH_3) (2.53 g, 10 mmol) by using potassium (0.975 g, 0.025 g atom) and sodium (0.575 g, 0.025 g atom) in a similar way to that described in procedure (B). The reaction mixture was filtered off and the solvent was removed *in vacuo*. The residual oil was washed with 1:1 aqueous tetrahydrofuran (10 ml) solution of satd $NaHCO_3$ and extracted with hexane. From the extracts, 1-trimethylsiloxy-1-trimethylsilyl-3-phenyl-1-propene (0.817 g, 29%) was isolated by fractional distillation. The aqueous layer was acidified with dil HCl and extracted three times with ether (10 ml). Removal of the solvent followed by bulb-to-bulb distillation afforded 3-phenylpropanethiocarboxylic acid (1.101 g, 66%). The product was identified by the following spectral data. IR (neat); 2525, 1685, and 1055 cm^{-1}. NMR (CCl_4); δ 2.78 (s, 4H, $C_6H_5C\underline{H}_2$-$C\underline{H}_2CO$–), 4.23 (s, 1H, –S<u>H</u>), and 7.02 (s, 5H, aromatic protons). MS; M^+ 166

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