Reactions of α,β-Unsaturated Ketone Acetals with Trimethylsilyl Cyanide and Trimethylsilyl Sulfides

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In the presence of a catalytic amount of trityl perchlorate, trimethylsilyl cyanide reacts with the dimethyl acetals of chalcone derivatives, with simultaneous double bond isomerization, to yield γ-methoxy-α,β-unsaturated carbonitriles. Trimethylsilyl sulfides react with dimethyl acetals derived from α,β-unsaturated ketones to yield 1,3-bis(alkylthio)propene derivatives under similar conditions.

In recent years, various reactions between acetals and a silylated nucleophile such as trimethylsilyl cyanide (TMS-CN),[1] silyl enol ethers,[2] ketene silyl acetals,[2] or allyltrimethylsilane[3] have been developed employing several efficient catalysts or promoters. Concerning the reaction of acetals derived from α,β-unsaturated ketones with silyl enol ethers, it was shown that either the Michael product or the β-alkoxy ketone was obtained, and that regioselectivity depends mostly on the reaction conditions.[4] It was also reported that a Lewis acid catalyst such as $SnCl_4$ or $BF_3 \cdot Et_2O$ promotes the reaction of acetals with TMS-CN and, in the case of the reaction of acetals derived from α,β-unsaturated ketones with TMS-CN, α-methoxy carbonitriles are obtained as major products.[1]

Recently, we have reported that, in the presence of a catalytic amount of transition metal salts such as $NiCl_2$, $CoCl_2$, or di-μ-chloro-bis(1,5-cyclooctadiene)-dirhodium ([Rh(COD)Cl]$_2$), TMS-CN reacts readily with various acetals under mild conditions.[5] During subsequent experiments, an interesting observation was made concerning the reaction of dimethyl acetals derived from α,β-unsaturated ketones: in the presence of 2 mol% of [Rh(COD)Cl]$_2$, TMS-CN reacts with (*E*)-chalcone dimethyl acetal to yield (*E*)-2-methoxy-2,4-diphenyl-3-butenenitrile, a normal cyanation product along with its isomerized product. The present study was initiated to examine in detail the reaction conditions required and the mechanism of this reaction in forming predominantly the isomerized product (*Z*)-4-methoxy-2,4-diphenyl-2-butenenitrile, briefly reported in preliminary communications.[6] This report describes in full the results of our investigation of the above reaction, and of a similar reaction employing another silylated nucleophile, trimethylsilyl sulfide, and of the reaction of the isomerized products thus obtained with several silylated nucleophiles.

Results and Discussion

Cyanation of Chalcone Dimethyl Acetal. We have already reported that when (*E*)-chalcone dimethyl acetal (**1**) was allowed to react with TMS-CN in the presence of 2 mol% of $CoCl_2$ in CH_2Cl_2 at room temperature for 18 h, (*E*)-2-methoxy-2,4-diphenyl-3-butenenitrile (**2**) was obtained in 99% yield.[5] On the other hand, **2** and its isomerized compound (**3**) were obtained in 89% yield when the above reaction was carried out in the presence of 2 mol% of [Rh(COD)Cl]$_2$ in CH_2Cl_2 at room temperature for 40 h (**2**:**3**=20:80, Scheme 1).[6] The structure of the above compound **3** was determined, mainly by ^{1}H and ^{13}C NMR measurement, to be (*Z*)-4-methoxy-2,4-diphenyl-2-butenenitrile as shown in Fig. 1. Concerning the geometry of the double bond in **3**, only one isomer was observed by ^{1}H and ^{13}C NMR measurement and we considered that it had the *Z*-configuration on the basis of the value of the coupling constant between the 1-position carbon and the 3-position proton ($^3J_{C1,H3}$=13.9 Hz) as measured by

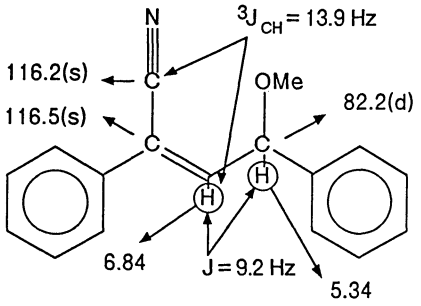
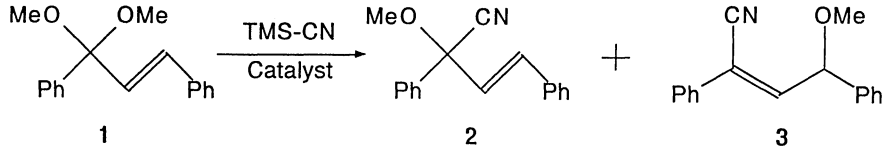


Fig. 1.



1 2 3

Scheme 1.

Table 1. Examination of Catalysts and Solvents[a]

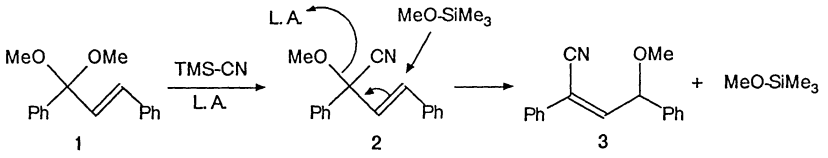
Entry	Catalyst[b]	Solvent	Time/h	Yield/%	Ratio of 2:3[c]
1[d]	$[Rh(COD)Cl]_2$	CH_2Cl_2	5	86	100: 0
2[d]	$[Rh(COD)Cl]_2$	CH_2Cl_2	10	83	64: 36
3[d]	$[Rh(COD)Cl]_2$	CH_2Cl_2	40	89	20: 80
4[d]	$[Rh(COD)Cl]_2$	CH_3CN	5	86	39: 61
5[d]	$[Rh(COD)Cl]_2$	CH_3CN	20	85	0:100
6	$NiCl_2$	CH_3CN	20	64	100: 0
7	$CoCl_2$	CH_3CN	20	83	81: 19
8	$Pd(acac)_2$	CH_3CN	20	77	100: 0
9	$Pd(OAc)_2$	CH_3CN	20	95	100: 0
10	$SnCl_2$	CH_3CN	3	98	96: 4
11	$BF_3 \cdot Et_2O$	CH_3CN	3	98	100: 0
12	$SnCl_4$	CH_3CN	3	Quant.	24: 76
13[e]	$AlCl_3$	CH_3CN	3	76	100: 0
14	$TiCl_4$	CH_3CN	3	97	88: 12
15	Ph_3CClO_4	CH_3CN	3	92	0:100
16	Ph_3CCl-$SnCl_2$[8]	CH_3CN	15	86	0:100
17	TMSCl-$SnCl_2$[9]	CH_3CN	15	85	0:100

a) Reactions were carried out using 1.5 equiv of TMS-CN at room temperature. b) Five mol% of catalyst was used except for Entries 1—5 and 13. c) Determined by ^1H NMR measurement. d) Two mol% of catalyst was used. e) Twenty-five mol% of catalyst was used.

Table 2. Isomerization from Isolated 2 to 3[a]

Entry	Reagent	Time/h	Ratio of 2:3[b]	Isolated yield of 3/%
1	Ph_3CClO_4 (5 mol%)	18	100: 0	—
2	Ph_3CClO_4 (5 mol%)-TMSOMe (2 equiv)	3	0:100	96
3	$SbCl_5$ (5 mol%)	3	8: 92	87
4	$SbCl_5$ (5 mol%)-TMSOMe (1.5 equiv)	1.5	0:100	83

a) Reactions were carried out in CH_3CN at room temperature. b) Determined by ^1H NMR measurement.



Scheme 2.

^{13}C NMR measurement (gated method).[7] In addition, the steric effect of the C2-phenyl group supports the above conclusion.

After experimentation with various reaction conditions, taking acetal **1** as a model substrate, it was found that **3** was obtained in good yield when the reaction was carried out in CH_3CN with the use of $[Rh(COD)Cl]_2$ or trityl perchlorate (Ph_3CClO_4) as catalyst (see Table 1).

Table 1 shows that, in the initial stage of the present reaction (after 5 h in CH_2Cl_2), cyanation gave only **2**, which in turn was isomerized to **3** when the mixture was kept standing for a long time. After a trial of various solvents, it was shown that CH_3CN is the best solvent, and isomerization from **2** to **3** was achieved within 20 h by using $[Rh(COD)Cl]_2$ as a catalyst. Isomerization proceeded slowly when such transition metal salts as $NiCl_2$, $CoCl_2$, $Pd(acac)_2$, or $Pd(OAc)_2$ was used as the catalyst. Very rapid isomerization took place when Ph_3CClO_4 was used, but the process was slower in the presence of generally known strong Lewis acids such as $BF_3 \cdot Et_2O$ and $AlCl_3$.

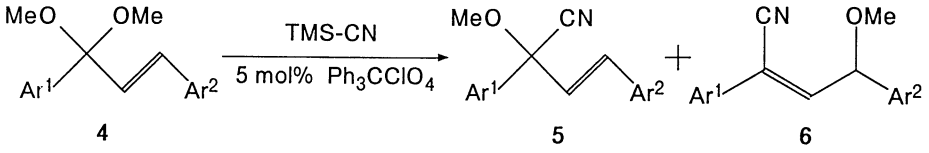
Concerning the mechanism of the isomerization, it is reasonable to consider that **3** was produced by the following reaction (Scheme 2). Trimethylsilyl methoxide (TMS-OMe), formed by the reaction of **1** with TMS-CN, would attack the 4-position carbon of **2** in the presence of a catalyst to result in the formation of a conjugated nitrile **3**.

Isomerization of isolated **2** to **3** was tried under various conditions (Table 2) and it was found that the isomerization did not occur in the presence of a catalytic amount of Ph_3CClO_4 alone, but was completed within 3 h in the presence of both 5 mol% of Ph_3CClO_4

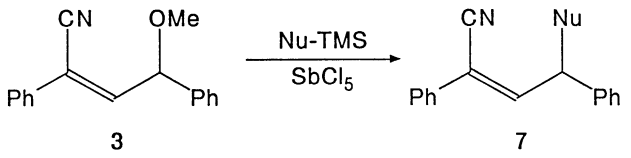
Table 3. Reactions of Dimethyl Acetals of Chalcone Derivatives with TMS-CN[a]

Entry	Ar^1	Ar^2	Time/h	Yield/%	Ratio of **5**:**6**[b]
1	Ph	Ph	3	92	0:100
2	*p*-Me-C_6H_4	Ph	5	98	0:100
3	*p*-MeO-C_6H_4	Ph	8	81	0:100
4	*p*-NO_2-C_6H_4	Ph	5	Quant.	82: 18
5	*p*-NO_2-C_6H_4	Ph	20	91	53: 47
6	Ph	*p*-NO_2-C_6H_4	5	42	100: 0
7	Ph	*p*-NO_2-C_6H_4	20	97	81: 19
8	Ph	1-Naphthyl	20	73	47: 53
9	Ph	2-Naphthyl	15	67	0:100
10	*p*-MeO-C_6H_4	*p*-NO_2-C_6H_4	20	94	0:100

a) Reactions were carried out using 1.5 equiv of TMS-CN and 5 mol% of Ph_3CClO_4 in CH_3CN at room temperature. b) Determined by ^1H NMR measurement.



Scheme 3.



Scheme 4.

Table 4. Reactions of **3** with Various Silylated Nucleophiles[a]

Entry	Nucleophile	Temp/°C	Yield/%
1	^{t}BuC(OSiMe$_3$)=CH_2	−78	96
2	PhC(OSiMe$_3$)=CH_2	−78	76
3	CH_2=$CHCH_2SiMe_3$	0	64[b]
4	TMS-CN	−23	87

a) Reactions were carried out using 1.5—1.8 equiv of nucleophiles and 1.1 equiv of $SbCl_5$ in CH_2Cl_2 for 1 h. b) Starting material **3** was recovered in 22%.

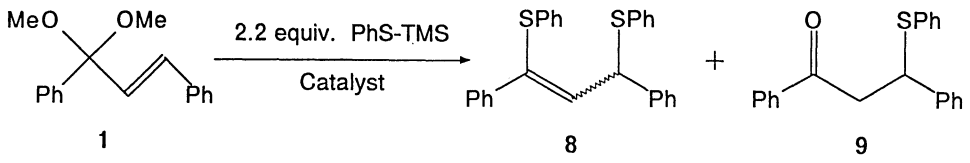
and 2 equiv of TMS-OMe. This result supported the validity of the above-described mechanism of the isomerization. With the use of $SbCl_5$ catalyst, a stronger Lewis acid, the isomerization took place even in the absence of TMS-OMe.

Similar reactions of various acetals of substituted chalcone derivatives with TMS-CN were tried in the presence of a catalytic amount of Ph_3CClO_4 (Scheme 3, Table 3). It is important to note, in these reactions, that the electronic effect of substituents contained in the aromatic rings of chalcone derivatives influences in the rate of isomerization. On the other hand, compounds having one or both of the phenyl groups in chalcone substituted with non-aromatic groups could be cyanated with TMS-CN to yield α-methoxy carbonitriles, but were not isomerized to γ-methoxy-α,β-unsaturated carbonitriles at all under similar conditions.

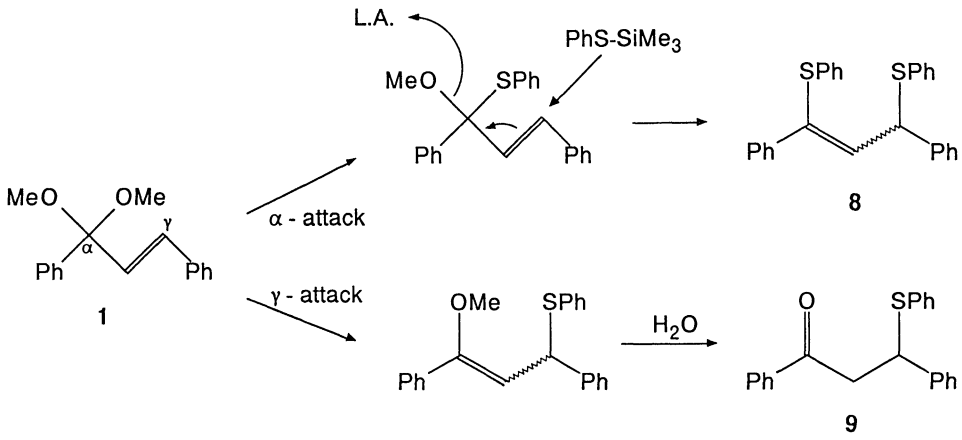
Concerning the utility of the isomerized compound **3** in the synthesis, it is thought that substitution by silylated nucleophiles at the allyl ether position[10] is possible in addition to the commonly known reactions of an α,β-unsaturated carbonitrile (Scheme 4). The reactions of **3** with several silylated nucleophiles under promotion by $SbCl_5$ are demonstrated in Table 4.

Reaction of Acetals Derived from α,β-Unsaturated Ketones with Trimethylsilyl Sulfide. In order to extend the scope of the above reaction, trimethylsilyl sulfide was employed as a silylated nucleophile instead of TMS-CN. It is well known that, in the presence of a catalytic amount of ZnI_2, aldehydes or ketones including α,β-unsaturated ketones react with trimethylsilyl sulfide to give the corresponding dithioacetals.[11] However, there have been few reports on the reaction of α,β-unsaturated ketone acetals with trimethylsilyl sulfide; for example, $AlCl_3$ promotes the above reaction to give 3-methoxyallyl sulfides or dithioacetals.[12] Firstly, acetal compound **1** was allowed to react with 2 equiv of phenylthiotrimethylsilane (PhS-TMS) in the presence of a catalytic amount of Ph_3CClO_4 in CH_3CN. It was found that 1,3-diphenyl-1,3-bis(phenylthio)-1-propene (**8**) (a mixture of *E*- and *Z*-isomers, 1:4), formed by isomerization of double bond, and 1,3-diphenyl-3-phenylthio-1-propanone (**9**), the Michael adduct, were obtained in 60 and 34% yields, respectively (Scheme 5). The dithioacetal of chalcone was not isolated under the above conditions.

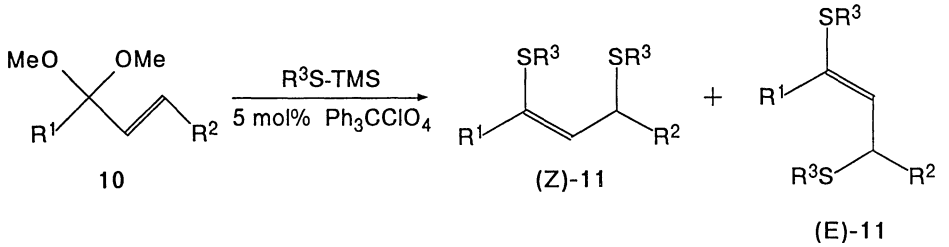
In order to increase the yield of the desired **8**, various reaction conditions (catalyst, solvent, temperature)



Scheme 5.



Scheme 6.



Scheme 7.

Table 5. Examination of Catalyst, Solvent, and Temperature[a)]

Entry	Catalyst	Solvent	Temp/°C	Yield/%	Ratio of **8**:**9**[b)]
1	$SnCl_4$	CH_3CN	R.T.	Quant.	70: 30
2	$SnCl_4$	CH_3CN	60	89	83: 17
3	$TiCl_4$	CH_3CN	R.T.	71	0:100
4	$TiCl_4$	CH_3CN	60	87	0:100
5	$EtAlCl_2$	CH_3CN	R.T.	98	76: 24
6[c)]	Ph_3CClO_4	CH_2Cl_2	−78	99	15: 85
7	Ph_3CClO_4	CH_2Cl_2	R.T.	Quant.	61: 39
8	Ph_3CClO_4	CH_3CN	R.T.	94	64: 36
9	Ph_3CClO_4	CH_3CN	60	Quant.	88: 12
10	Ph_3CClO_4	Toluene	60	84	100: 0
11	Ph_3CClO_4	Benzene	60	98	100: 0

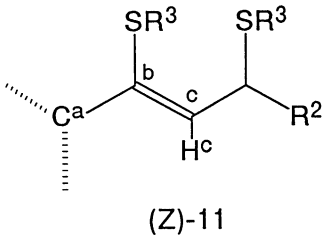
a) Reactions were carried out using 2.2 equiv of PhS-TMS and 5 mol% of catalyst for 3 h except for Entry 6. b) Determined by preparative TLC (silica gel). Ratio of *E*:Z in **8** was 1:9—3:7 (determined by ^1H MMR measurement). c) Reaction time was 8 h.

were examined (Table 5), and the ratio of **8** to **9** was found to be increased by raising the reaction temperature. Eventually **8** was obtained in good yield without the accompanying by-product **9** when the reaction was carried out using 5 mol% of Ph_3CClO_4 in benzene or toluene at 60 °C (Entries 10 and 11). On the other hand, the Michael adduct **9**, was obtained mainly when the reaction was carried out at −78 °C (Entry 6). In this reaction, PhS-TMS could attack either on the α- or the γ-position of acetal **1** (Scheme 6). In the former possibility, 3-methoxy-3-phenylthio-1-propene would be formed and be attacked by one more PhS-

Table 6. Reactions of α,β-Unsaturated Ketone Acetals with Trimethylsilyl Sulfide[a]

Entry		Substrate		Sulfide	Yield of	Ratio of
		R^1	R^2	R^3	**11**/%	$E:Z$[b]
1	**10a**	Ph	Ph	Ph	96	12: 88
2	**10a**	Ph	Ph	Et	96	23: 77
3	**10b**	^{t}Bu	Ph	Ph	93	0:100
4	**10b**	^{t}Bu	Ph	Et	77	0:100
5	**10c**	Ph	^{t}Bu	Ph	99	59: 41
6	**10c**	Ph	^{t}Bu	Et	69	4: 96
7	**10d**	Ph	COOMe	Ph	87	25: 75
8	**10d**	Ph	COOMe	Et	77	25: 75
9	**10e**	p-NO_2-C_6H_4	p-MeO-C_6H_4	Et	65	15: 85
10	**10f**	Me	COOMe	Ph	77	38: 62

a) Reactions were carried out using 2.2—2.4 equiv of sulfide and 5 mol% of Ph_3CClO_4 in benzene at 60 °C for 0.5—2 h. b) Determined by ^{1}H NMR measurement.



(Z)-11

Fig. 2.

TMS only at the γ-position because of steric hindrance which would result in the formation of isomerized compound **8**. In the latter, the 1-methoxy-3-phenylthio-1-propene formed would not react further, so that the Michael adduct **9**, would be obtained after quenching with water.

Next, similar reactions of various acetals of α,β-unsaturated ketones with PhS-TMS or EtS-TMS were tried in the presence of a catalytic amount of Ph_3CClO_4 in benzene at 60 °C (Scheme 7, Table 6). Isomerized compound **11** was obtained under the above conditions and the ratio between (*E*)-**11** and (*Z*)-**11** was influenced by the structure of **10**. The geometries of the double bond in **11** are considered to be as follows: (1) in Entries 1, 2, and 5—9, the isomer in which an olefinic proton (H^c in Fig. 2) occurs in a lower field on ^{1}H NMR measurement was considered to be a *Z*-isomer; (2) in Entries 3 and 4, only one isomer was obtained and it was thought to be a *Z*-isomer because of the steric hindrance of the ^{t}Bu group; (3) in Entries 9 and 10, the isomer in which a signal of a carbon atom bonded to the double bond (C^a in Fig. 2) occurs in a lower field on ^{13}C NMR measurement suggested the *Z*-configuration.

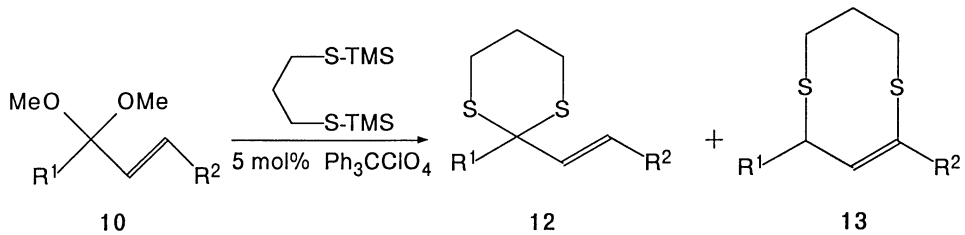
It is interesting to note that the compounds **10b—d**, and **10f**, which have a *t*-butyl or methoxycarbonyl group instead of a phenyl group in the chalcone (and which could be cyanated with TMS-CN to yield α-methoxy carbonitriles, but were not isomerized to γ-methoxy-α,β-unsaturated carbonitriles at all under conditions similar to those mentioned in the previous section), were also readily converted to the corresponding isomerized products **11**. On the other hand, when these acetals were treated with 1,3-bis(trimethylsilylthio)propane under similar conditions (Scheme 8), it was found that only dithiane **12** was obtained from **10a**, and the mixtures of **12** and 1,5-dithia-2-cyclooctene derivative **13** were obtained from **10b** or **10c** (Table 7).

In relation to the utility of the isomerized compounds **11**, it was considered that allyl sulfides could

Table 7. Reactions of α,β-Unsaturated Ketone Acetals with $Me_3SiS(CH_2)_3SSiMe_3$[a]

Entry	R^1	R^2	Yield/%	Ratio of **12**:**13**[b]
1	Ph	Ph	70	100: 0
2	^{t}Bu	Ph	87	56:44
3	Ph	^{t}Bu	72	43:57

a) Reactions were carried out using 1.1 equiv of sulfide and 5 mol% of Ph_3CClO_4 in benzene at 60 °C for 2—3 h. b) Determined by ^{1}H MMR measurement.



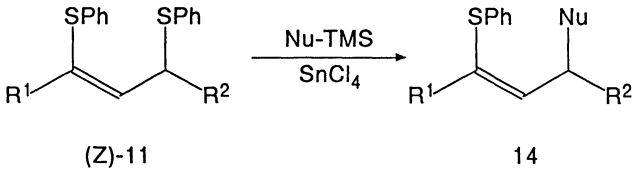
10 12 13

Scheme 8.

Table 8. Reactions of (**Z**)-**11** with Various Silylated Nucleophiles[a)]

Entry	R^1	R^2	Nucleophile	Temp/°C	Yield/%
1	^{t}Bu	Ph	^{t}BuC(OSiMe$_3$)=CH$_2$	0	84
2	^{t}Bu	Ph	PhC(OSiMe$_3$)=CH$_2$	0	72
3	^{t}Bu	Ph	Et$_3$SiH	0	74
4	^{t}Bu	Ph	CH$_2$=CHCH$_2$SiMe$_3$	R.T.	74
5	Ph	Ph	^{t}BuC(OSiMe$_3$)=CH$_2$	0	92
6	Ph	Ph	PhC(OSiMe$_3$)=CH$_2$	0	97
7	Ph	Ph	Et$_3$SiH	0	69
8	Ph	COOMe	PhC(OSiMe$_3$)=CH$_2$	R.T.	54

a) Reactions were carried out using 1.5—1.8 equiv of nucleophile and 1.1 equiv of $SnCl_4$ in CH_2Cl_2 for 0.5—1 h.



(Z)-11 14

Scheme 9.

be activated toward silylated nucleophiles by means of a Lewis acid. It is already known that dithioacetals reacted with silyl enol ethers in the presence of Ph_3CBF_4[13)] and that the allylic methoxyl group of **3** is replaced by silylated nucleophiles in the presence of $SbCl_5$, as mentioned in the previous section. Substitution at the 3-position of **11** with several silylated nucleophiles (Scheme 9) was therefore tried and it was found that $SnCl_4$, promotes the reaction of **11** with the silylated nucleophiles, as shown in Table 8.

In conclusion, it is noted that in the presence of a catalytic amount of Ph_3CClO_4, TMS-CN reacts with dimethyl acetals derived from chalcone derivatives, with simultaneous double bond isomerization, to yield γ-methoxy-α,β-unsaturated carbonitriles; and trimethylsilyl sulfides react with dimethyl acetals derived from α,β-unsaturated ketones to yield 1,3-bis(alkylthio)propene derivatives under similar conditions.

This type of reaction accompanying isomerization of a double bond opens up new possibilities, especially in the synthesis of olefin derivatives.

Experimental

All melting points were uncorrected. The IR spectra were determined on a Hitachi 270-30 or JASCO IRA-2 spectrometer. The NMR spectra were recorded with a Hitachi R-24B, a JEOL FX90Q, a JEOL GSX-400 or a JEOL GSX-500 spectrometer in $CDCl_3$ with tetramethylsilane as an internal standard. The mass spectra were taken on a JEOL JMS-HX110 or a JEOL JMS-D300. Dichloromethane and acetonitrile were distilled from P_2O_5, and then distilled from CaH_2 and stored over Molecular Sieves. Benzene and toluene were dried over $CaCl_2$, then distilled from P_2O_5 and stored over Molecular Sieves. Purification of products was performed by column chromatography on silica gel (Merck, Art. 7734 Kieselgel 60) or preparative TLC on silica gel (Wakogel B-5F).

Dimethyl acetals were prepared by transacetalization of the corresponding ketones with trimethyl orthoformate in the presence of *p*-TsOH·H_2O, and purified by distillation or recrystallization. Trimethylsilyl cyanide, allyltrimethylsilane, and triethylsilane were purified by distillation. Trimethylsilyl sulfides were prepared by silylation of the corresponding lithium salts of mercaptans. Silyl enol ethers were prepared by silylation of the corresponding enolates of ketones, and purified by distillation.

Preparation of γ-Methoxy-α,β-unsaturated Carbonitriles (6) (Table 3). A typical reaction procedure is described for (*E*)-chalcone dimethyl acetal (**1**) with TMS-CN by the use of Ph_3CClO_4, as a catalyst (Entry 1): In an argon atmosphere, Ph_3CClO_4 (3.4 mg, 0.01 mmol) and TMS-CN (34.7 mg, 0.350 mmol) were stirred in acetonitrile (3 ml) at room temperature for 15 min, and to the mixture was added (*E*)-chalcone dimethyl acetal (52.9 mg, 0.208 mmol) in acetonitrile (1 ml). The reaction mixture was stirred for 3 h at room temperature, then quenched with pH 7 phosphate buffer. The organic materials were extracted with ethyl acetate and the combined extract was dried over Na_2SO_4. After evaporation of the solvent, the residue was purified by preparative TLC (silica gel, hexane : AcOEt=5 : 1) to afford (*Z*)-4-methoxy-2,4-diphenyl-2-butenenitrile (**3**) (47.9 mg, 0.192 mmol, 92%). IR (neat) 2220, 1495, 1450, 1085, 755, 690 cm^{-1}; ^{1}H NMR δ=3.43 (3H, s), 5.34 (1H, d, *J*=9.2 Hz), 6.84 (1H, d, *J*=9.2 Hz), 7.3—7.6 (10H, m); ^{13}C NMR δ=56.8 (q), 82.2 (d), 116.2 (s), 116.5 (s), 126.0 (d), 126.6 (d), 128.6 (d), 129.0 (d and d, 2C), 129.7 (d), 132.3 (s), 139.1 (s), 144.9 (d); MS *m/z* 249 (M$^+$), 217, 140, 121, 105. Found: *m/z* 249.1124. Calcd for $C_{17}H_{15}NO$: M, 249.1154.

In Entries 4 and 5, the isomerization from **5** to **6** was not achieved completely, and pure **6** was obtained by preparative TLC. Other analytical data of **6** follow.

(Z)-4-Methoxy-2-(4-methylphenyl)-4-phenyl-2-butenenitrile (Entry 2). IR (neat) 2220, 1450, 1085, 750 cm^{-1}; ^{1}H NMR δ=2.35 (3H, s), 3.43 (3H, s), 5.33 (1H, d, *J*=9.2 Hz), 6.79 (1H, d, *J*=9.2 Hz), 7.18 (2H, d, *J*=8.3 Hz), 7.3—7.5 (7H, m); ^{13}C NMR δ=21.2 (q), 56.8 (q), 82.1 (d), 116.3 (s), 116.4 (s), 125.8 (d), 126.5 (d), 128.5 (d), 128.9 (d), 129.3 (s), 129.7 (d), 139.2 (s), 139.9 (s), 143.7 (d); MS, *m/z* 263 (M$^+$), 248, 231, 216. Found: *m/z* 263.1304. Calcd for $C_{18}H_{17}NO$: M, 263.1310.

(Z)-4-Methoxy-2-(4-methoxyphenyl)-4-phenyl-2-butenenitrile (Entry 3). IR (neat) 2210, 1605, 1515, 1255, 1180, 1085 cm^{-1}; ^{1}H NMR δ=3.43 (3H, s), 3.81 (3H, s), 5.32 (1H, d, *J*=9.2 Hz), 6.70 (1H, d, *J*=9.2 Hz), 6.89 (2H, d, *J*=8.2 Hz), 7.3—7.5 (7H,

m); ^{13}C NMR δ=55.4 (q), 56.7 (q), 82.2 (d), 114.4 (d), 116.1 (s), 116.4 (s), 124.8 (s), 126.5 (d), 127.4 (d), 128.5 (d), 128.9 (d), 139.4 (s), 142.5 (d), 160.7 (s); MS m/z 279 (M^+), 264, 248, 176. Found: m/z 279.1263. Calcd for $C_{18}H_{17}NO_2$: M, 279.1259.

(*Z*)-4-Methoxy-2-(4-nitrophenyl)-4-phenyl-2-butenenitrile (Entry 4). Mp 110—112 °C; IR (KBr) 2220, 1600, 1515, 1340, 1120, 1095, 855, 750 cm^{-1}; ^{1}H NMR δ=3.43 (3H, s),5.35 (1H, d, J=9.2 Hz), 7.03 (1H, d, J=9.2 Hz), 7.35—7.5 (5H, m), 7.72 (2H, d, J=9.2 Hz), 8.25 (2H, d, J=9.2 Hz); ^{13}C NMR δ=56.9 (q), 82.2 (d), 114.3 (s), 115.3 (s), 124.3 (d), 126.7 (d), 126.9 (d), 129.0 (d), 129.2 (d), 138.3 (s), 148.3 (s), 148.9 (d); MS m/z 294 (M^+), 279, 263, 217. Found: C, 69.25; H, 4.76; N, 9.56%. Calcd for $C_{17}H_{14}N_2O_3$: C, 69.38; H, 4.79; N, 9.52%.

(*Z*)-4-Methoxy-4-(4-nitrophenyl)-2-phenyl-2-butenenitrile (Entry 5). IR (neat) 2200, 1605, 1595, 1525, 1350, 1080 cm^{-1}; ^{1}H NMR δ=3.49 (3H, s), 5.46 (1H, d, J=9.2 Hz), 6.74 (1H, d, J=9.2 Hz), 7.41 (3H, m), 7.56 (2H, m), 7.66 (2H, d, J=9.2 Hz), 8.26 (2H, d, J=8.2 Hz); ^{13}C NMR δ=57.2 (q), 81.1 (d), 116.0 (s), 118.1 (s), 124.2 (d), 126.1 (d), 127.3 (d), 129.2 (d), 130.2 (d), 131.7 (s), 143.1 (d), 146.2 (s), 148.0 (s); MS m/z 294 (M^+), 277, 262, 247, 217. Found: m/z 294.1001. Calcd for $C_{17}H_{14}N_2O_3$: M, 294.1004.

(*Z*)-4-Methoxy-4-(1-naphthyl)-2-phenyl-2-butenenitrile (Entry 6). IR (neat) 2210, 1600, 1510, 1450, 1085, 780, 760 cm^{-1}; ^{1}H NMR δ=3.50 (3H, s), 5.93 (1H, d, J=9.2 Hz), 7.06 (1H, d, J=9.2 Hz), 7.35 (3H, m), 7.5—7.6 (5H, m), 7.73 (1H, d, J=7.3 Hz), 7.85 (1H, d, J=8.3 Hz), 7.89 (1H, d, J=8.3 Hz), 8.36 (1H, d, J=8.3 Hz); ^{13}C NMR δ=56.9 (q), 80.6 (d), 116.2 (s), 117.2 (s), 123.6 (d), 125.5 (d), 125.6 (d), 126.0 (d), 126.1 (d), 126.8 (d), 129.0 (d and d, 2C), 129.3 (d), 129.7 (d), 130.8 (s), 132.3 (s), 134.1 (s), 134.7 (s), 144.2 (d); MS m/z 299 (M^+), 284, 267, 241, 155. Found: m/z 299.1280. Calcd for $C_{21}H_{17}NO$: M, 299.1310.

(*Z*)-4-Methoxy-4-(2-naphthyl)-2-phenyl-2-butenenitrile (Entry 7). IR (neat) 2210, 1600, 1450, 1080, 750 cm^{-1}; ^{1}H NMR δ=3.48 (3H, s), 5.51 (1H, d, J=9.2 Hz), 6.92 (1H, d, J=9.2 Hz), 7.3—7.6 (8H, m) , 7.8—7.9 (3H, m), 7.95 (1H, s); ^{13}C NMR δ=56.9 (q), 82.3 (d), 116.3 (s), 116.6 (s), 124.0 (d), 125.9 (d), 126.0 (d), 126.4 (d), 126.5 (d), 127.8 (d), 128.1 (d), 129.0 (d and d, 2C), 129.7 (d), 132.3 (s), 133.4 (s), 136.4 (s), 144.7 (d); MS m/z 299 (M^+), 284, 268, 241, 155. Found: m/z 299.1306. Calcd for $C_{21}H_{17}NO$: M, 299.1310.

(*Z*)-4-Methoxy-2-(4-methoxyphenyl)-4-(4-nitrophenyl)-2-butenenitrile (Entry 8). IR (neat) 2200, 1605, 1515, 1350, 1250, 1180, 825 cm^{-1}; ^{1}H NMR δ=3.48 (3H, s), 3.83 (3H, s), 5.43 (1H, d, J=9.2 Hz), 6.59 (1H, d, J=9.2 Hz), 6.92 (2H, d, J=9.2 Hz), 7.50 (2H, d, J=8.3 Hz), 7.65 (2H, d, J=9.2 Hz), 8.25 (2H, d, J=8.3 Hz); ^{13}C NMR δ=55.5 (q), 57.1 (q), 81.2 (d), 114.5 (d), 116.1 (5), 117.7 (s), 124.2 (d), 127.2 (d), 127.5 (d), 140.5 (d), 146.5 (s), 147.9 (s), 161.1 (s); MS m/z 324 (M^+), 307, 293, 150. Found: m/z 324.1112. Calcd for $C_{18}H_{16}N_2O_4$: M, 324.1110.

The α-methoxy carbonitrile **5** corresponding to **6** was obtained by the reaction of the corresponding acetal **4** and TMS-CN (1.5 equiv) in the presence of 2 mol% of $CoCl_2$ in CH_2Cl_2.[5a] ^{1}H and ^{13}C NMR data of **5** follow.

(*E*)-2-Methoxy-2,4-diphenyl-3-butenenitrile (Entry 1). ^{1}H NMR δ=3.47 (3H, s), 6.18 (1H, d, J=15.6 Hz), 7.01 (1H, d, J=15.6 Hz), 7.3—7.5 (8H, m), 7.59 (2H, m); ^{13}C NMR δ=53.9 (q), 81.2 (s), 117.2 (s), 126.1 (d), 127.1 (d and d, 2C), 128.8 (d), 128.9 (d), 129.0 (d), 129.3 (d), 133.5 (d), 135.0 (s), 137.4 (s).

(*E*)-2-Methoxy-2-(4-methylphenyl)-4-phenyl-3-butenenitrile (Entry 2). ^{1}H NMR δ=2.37 (3H, s), 3.45 (3H, s), 6.18 (1H, d, J=15.6 Hz), 6.98 (1H, d, J=15.6 Hz), 7.23 (2H, d, J=7.3 Hz), 7.3 (3H, m), 7.41 (2H, d, J=7.3 Hz), 7.46 (2H, d, J=8.3 Hz); ^{13}C NMR δ=21.1 (q), 53.8 (q), 81.1 (s), 117.3 (s), 126.0 (d), 127.1 (d), 127.2 (d), 128.7 (d), 128.8 (d), 129.6 (d), 133.3 (d), 134.4 (s), 135.0 (s), 139.3 (s).

(*E*)-2-Methoxy-2-(4-methoxyphenyl)-4-phenyl-3-butenenitrile (Entry 3). ^{1}H NMR δ=3.44 (3H, s), 3.83 (3H, s), 6.18 (1H, d, J=15.6 Hz), 6.94 (2H, d, J=9.2 Hz), 6.97 (1H, d, J=16 Hz), 7.28—7.36 (3H, m), 7.41 (2H, m), 7.50 (2H, d, J=9.2 Hz); ^{13}C NMR δ=53.8 (q), 55.4 (q), 80.7 (s), 114.3 (d), 117.3 (s), 127.1 (d), 127.2 (d), 127.5 (d), 128.8 (d and d, 2C), 129.3 (s), 133.3 (d), 135.0 (s), 160.3 (s).

(*E*)-2-Methoxy-2-(4-nitrophenyl)-4-phenyl-3-butenenitrile (Entry 4). ^{1}H NMR δ=3.54 (3H, s), 6.07 (1H, d, J=15.6 Hz), 7.11 (1H, d, J=15.6 Hz), 7.3—7.45 (5H, m), 7.79 (2H, d, J=8.3 Hz), 8.29 (2H, d, J=8.3 Hz); ^{13}C NMR δ=54.2 (q), 80.6 (s), 116.3 (s), 124.2 (d), 125.4 (d), 127.1 (d), 127.2 (d), 128.9 (d), 129.4 (d), 134.3 (s), 135.2 (d), 144.5 (s), 148.4 (s).

(*E*)-2-Methoxy-4-(4-nitrophenyl)-2-phenyl-3-butenenitrile (Entry 5). ^{1}H NMR δ=3.47 (3H, s), 6.36 (1H, d, J=16.5 Hz), 7.05 (1H, d, J=15.6 Hz), 7.4—7.6 (7H, m), 8.20 (2H, d, J=9.2 Hz); ^{13}C NMR δ=54.1 (q), 81.0 (s), 116.7 (s), 124.1 (d), 126.1 (d), 127.8 (d), 129.2 (d), 129.7 (d), 130.7 (d), 131.7 (d), 136.3 (s), 141.3 (s), 147.7 (s).

(*E*)-2-Methoxy-4-(1-naphthyl)-2-phenyl-3-butenenitrile (Entry 6). ^{1}H NMR δ=3.54 (3H, s), 6.24 (1H, d, J=15.6 Hz), 7.4—7.9 (12H, m), 8.10 (1H, d, J=8.3 Hz); ^{13}C NMR δ=54.0 (q), 81.3 (s), 117.3 (s), 123.5 (d), 124.4 (d), 125.5 (d), 126.1 (d and d, 2C), 126.6 (d), 128.6 (d), 129.0 (d), 129.1 (d), 129.4 (d), 130.1 (d), 130.9 (d), 131.2 (s), 132.7 (s), 133.6 (s), 137.3 (s).

(*E*)-2-Methoxy-4-(2-naphthyl)-2-phenyl-3-butenenitrile (Entry 7). ^{1}H NMR δ=3.50 (3H, s), 6.30 (1H, d, J=16.5 Hz), 7.16 (1H, d, J=15.6 Hz), 7.4—7.5 (5H, m), 7.56 (1H, m), 7.62 (2H, m), 7.80 (4H, m); ^{13}C NMR δ=54.0 (q), 81.3 (s), 117.2 (s), 123.4 (d), 126.1 (d), 127.3 (d), 127.7 (d), 127.9 (d), 128.2 (d), 128.5 (d), 129.0 (d), 129.3 (d), 132.4 (s), 133.4 (s), 133.5 (s), 133.6 (d), 137.4 (s).

(*E*)-2-Methoxy-2-(4-methoxyphenyl)-4-(4-nitrophenyl)-3-butenenitrile (Entry 8). ^{1}H NMR δ=3.43 (3H, s), 3.84 (3H, s), 6.37 (1H, d, J=16.5 Hz), 6.97 (2H, d, J=9.2 Hz), 7.02 (1H, d, J=16.5 Hz), 7.49 (2H, d, J=9.2 Hz), 7.55 (2H, d, J=9.2 Hz), 8.19 (2H, d, J=9.2 Hz); ^{13}C NMR δ=54.0 (q), 55.4 (q), 80.5 (s), 114.5 (d), 116.8 (s), 124.1 (d), 127.6 (d), 127.7 (d), 128.1 (s), 130.4 (d), 131.9 (d), 141.4 (s), 147.7 (s), 160.6 (s).

Isomerization from Isolated 2 to 3. The following is a description of a typical procedure for isomerization in the presence of Ph_3CClO_4 and TMS-OMe (Entry 2): In an argon atmosphere, Ph_3CClO_4 (3.2 mg, 0.009 mmol) and TMS-OMe (42.7 mg, 0.410 mmol) were stirred in CH_3CN (2 ml) for 10 min at room temperature, and then (*E*)-2-methoxy-2,4-diphenyl-3-butenenitrile (**2**) (47.8 mg, 0.192 mmol) in CH_3CN (1 ml) was added. The reaction mixture was stirred for 3 h at room temperature and quenched with an aqueous solution of $NaHCO_3$. The organic materials were extracted with ethyl acetate and the combined extract was dried over Na_2SO_4. After evaporation of the solvent, the residue was purified by preparative TLC (silica gel, hexane : AcOEt=7 : 1) to afford (*Z*)-4-methoxy-2,4-diphenyl-2-butenenitrile (**3**) (46.1 mg, 0.185 mmol, 96%).

Reaction of 3 with Silylated Nucleophiles (Table 4). A typical procedure for the reaction of **3** with trimethylsilyl enol ether of *t*-butyl methyl ketone (Entry 1) follows: In an argon atmosphere, (*Z*)-4-methoxy-2,4-diphenyl-2-butenenitrile

(**3**) (49.1 mg, 0.197 mmol) and the trimethylsilyl enol ether of *t*-butyl methyl ketone (57.0 mg, 0.331 mmol) were dissolved in CH_2Cl_2 (2 ml). The solution was cooled to −78 °C, and 0.5 M $SbCl_5$ solution (1 M=1 mol dm^{-3}) in CH_2Cl_2 (0.44 ml, 0.22 mmol) was added. The reaction mixture was stirred for 1 h at −78 °C and quenched with an aqueous solution of $NaHCO_3$. The organic materials were extracted with CH_2Cl_2 and the combined extract was dried over Na_2SO_4. After evaporation of the solvent, the residue was purified by preparative TLC (silica gel, hexane : AcOEt=5 : 1) to afford (*Z*)-7,7-dimethyl-6-oxo-2,4-diphenyl-2-octenenitrile (59.9 mg, 0.189 mmol, 96%); mp 101—103 °C; IR (KBr) 2220, 1700, 1475, 1455, 1070, 760, 695 cm^{-1}; ^{1}H NMR δ=1.03 (9H, s), 2.98 (2H, m), 4.4 (1H, m), 6.82 (1H, d, *J*=10 Hz), 7.2 (10H, m). Found: C, 83.03; H, 7.51; N, 4.37%. Calcd for $C_{22}H_{23}NO$: C, 83.24; H, 7.30; N, 4.41%.

Other analytical data are presented below.

(*Z*)-6-Oxo-2,4,6-triphenyl-2-hexenenitrile (Entry 2). Mp 117—118 °C; IR (KBr) 2220, 1750, 1450, 1210, 750, 690 cm^{-1}; ^{1}H NMR δ=3.52 (2H, d, *J*=7 Hz), 4.70 (1H, dt, *J*=10 Hz, 7 Hz), 6.80 (1H, d, *J*=10 Hz), 7.1—7.4 (8H, m), 7.77 (2H, m) Found: C, 85.20; H, 5.93; N, 4.10%. Calcd for $C_{24}H_{19}NO$: C, 85.43; H, 5.68; N, 4.15%.

(*Z*)-2,4-Diphenyl-2,6-heptadienenitrile (Entry 3). IR (neat) 2210, 1640, 1600, 1495, 1450, 915, 755, 695 cm^{-1}; ^{1}H NMR δ=2.55 (2H, t, *J*=7 Hz), 3.99 (1H, dt, *J*=10 Hz, 7 Hz), 4.8—5.1 (2H, m), 5.5 (1H, m), 6.58 (1H, d, *J*=10 Hz), 7.1 (10H, m); MS *m/z* 259 (M$^+$), 218, 191. Found: *m/z* 259.1335. Calcd for $C_{19}H_{17}N$: M, 259.1361.

(*Z*)-2,4-Diphenyl-2-pentene-1,5-dinitrile (Entry 4). IR (neat) 2230, 2210, 1600, 1495, 1450, 755, 690 cm^{-1}; ^{1}H NMR δ=5.00 (1H, d, *J*=10 Hz), 6.55 (1H, d, *J*=10 Hz), 7.2 (10H, m).

Reaction of α,β-Unsaturated Ketone Acetals with Trimethylsilyl Sulfides (Table 6). A typical procedure for the reaction of (*E*)-chalcone dimethyl acetal **1** with PhS-TMS (Entry 1) was as follows.

In an argon atmosphere, Ph_3CClO_4 (5.4 mg, 0.016 mmol) was suspended in benzene (1 ml), to which was added PhS-TMS (135.0 mg, 0.740 mmol) in benzene (1 ml). The reaction mixture was heated to 60 °C and stirred for 30 min, and (*E*)-chalcone dimethyl acetal (79.7 mg, 0.314 mmol) in benzene (1 ml) was then added over a 5 min period. The reaction mixture was stirred for 3 h at 60 °C and quenched with aqueous $NaHCO_3$ solution. The organic materials were extracted with ethyl acetate and the combined extract was dried over Na_2SO_4. After evaporation of the solvent, the residue was purified by preparative TLC (silica gel, hexane : ether=93 : 7) to afford 1,3-diphenyl-1,3-bis (phenylthio)propene (123.8 mg, 0.302 mmol, 96%) as a mixture of *E*- and *Z*-isomer (*E* : *Z*=12 : 88). Pure *Z*-isomer was obtained by recrystallization from ethanol (90.1 mg).

***Z*-Isomer:** Mp 103—105 °C; IR (KBr) 1580, 1480, 1440, 750, 735, 695 cm^{-1}; ^{1}H NMR δ=5.85 (1H, d, *J*=10.1 Hz), 6.59 (1H, d, *J*=10.1 Hz), 6.8—7.55 (20H, m); ^{13}C NMR δ=53.3 (d), 125.8 (d), 127.6 (d), 127.8 (d), 127.9 (d), 128.0 (d), 128.1 (d), 128.5 (d), 128.8 (d), 128.9 (d), 129.2 (d), 133.7 (d), 134.2 (s), 134.5 (s), 135.8 (s), 137.2 (d), 139.2 (s), 139.8 (s); MS *m/z* 410 (M$^+$), 301. Found: C, 79.28; H, 5.23; S, 15.63%. Calcd for $C_{27}H_{22}S_2$: C, 78.98; H, 5.40; S, 15.62%.

***E*-Isomer:** ^{1}H NMR δ=4.90 (1H, d, *J*=11.0 Hz), 6.13 (1H, d, *J*=11.0 Hz), 7.00 (2H, m), 7.15—7.35 (18H, m); ^{13}C NMR δ=52.7 (d), 127.4 (d), 127.5 (d), 127.7 (d), 127.9 (d), 128.7 (d), 128.9 (d), 129.3 (d), 130.3 (d), 132.4 (d), 133.3 (s), 134.0 (d), 136.8 (s), 137.8 (s), 139.9 (s).

Other analytical data are shown below.

1,3-Bis(ethylthio)-1,3-diphenylpropene. (*E* : *Z*=23 : 77, mixture) (Entry 2). IR (neat) 1600, 1495, 1450, 1255, 820 cm^{-1}; ^{1}H NMR δ=1.02 and 1.06 (3H, 23 : 77, t, *J*=7.3 Hz), 1.18 and 1.31 (3H, 23 : 77, t, *J*=7.3 Hz), 2.33 and 2.40 (2H, 23 : 77, q, *J*=7.3 Hz), 2.5 (2H,m), 4.57 (0.23×1H, d, *J*=10.8 Hz), 5.47 (0.77×1H, d, *J*=9.8 Hz), 6.03 (0.23×1H, d, *J*=10.7 Hz), 6.23 (0.77×1H, d, *J*=9.8 Hz), 7.2—7.55 (10H, m); ^{13}C NMR δ=14.1 (q, *E*), 14.5 (q, *E*), 15.0 (q, *Z*), 15.1 (q, *Z*), 25.4 (t, *E*), 25.5 (t, *Z*), 26.0 (t, *E*), 26.4 (t, *Z*), 47.8 (d, *E*), 48.3 (d, *Z*), 127.2 (d, *Z*), 127.8 (d, *Z*), 128.0 (d, *Z*), 128.3 (d, *Z*), 128.7 (d, *Z*), 129.3 (d, *Z*), 135.0 (d, *Z*), 137.3 (s, *Z*), 139.4 (s, *Z*), 140.9 (s, *Z*), 141.0 (s, *E*); MS *m/z* 314 (M$^+$), 286, 270, 253. Found: *m/z* 253.1022. Calcd for $C_{17}H_{17}S$: M−SEt, 253.1051.

(*Z*)-4,4-Dimethyl-1-phenyl-1,3-bis(phenylthio)-2-pentene (Entry 3). Mp 105—108 °C; IR (KBr) 1580, 1480, 1440, 740, 690 cm^{-1}; ^{1}H NMR δ=1.04 (9H, s), 5.46 (1H, d, *J*=10.1 Hz), 6.47 (1H, d, *J*=10.1 Hz), 6.8—7.5 (15H, m); ^{13}C NMR δ=29.4 (q), 39.6 (s), 53.3 (d), 124.8 (d), 126.7 (d), 127.3 (d), 127.7 (d), 128.0 (d), 128.4 (d), 128.6 (d and d, 2C), 133.9 (s), 134.1 (d), 135.8 (d), 137.9 (s), 139.5 (s), 143.6 (s); MS *m/z* 390 (M$^+$), 281. Found: C, 77.00; H, 6.57; S, 16.11%. Calcd for $C_{25}H_{26}S_2$: C, 76.87; H, 6.71; S, 16.42%.

(*Z*)-1,3-Bis(ethylthio)-4,4-dimethyl-1-phenyl-2-pentene (Entry 4). IR (neat) 1600, 1455, 1265, 690 cm^{-1}; ^{1}H NMR δ=1.18 (3H, t, *J*=7.3 Hz), 1.19 (9H, s), 1.26 (3H, t, *J*=7.3 Hz), 2.35—2.65 (4H,m), 5.41 (1H, d, *J*=10.2 Hz), 6.20 (1H, d, *J*=10.2 Hz), 7.2—7.45 (5H, m); ^{13}C NMR δ=14.8 (q), 15.1 (q), 25.5 (t), 29.5 (q), 31.9 (t), 39.6 (s), 48.7 (d), 127.1 (d), 127.8 (d), 128.6 (d), 133.3 (d), 141.0 (s), 147.3 (s); MS *m/z* 294 (M$^+$), 278, 233,210. Found: *m/z* 294.1482. Calcd for $C_{17}H_{26}S_2$: M, 294.1476.

4,4-Dimethyl-1-phenyl-1,3-bis(phenylthio)-1-pentene (*E* : *Z*= 59 : 41, mixture) (Entry 5). IR (neat) 1580, 1480, 1440, 1370, 1025, 740, 690 cm^{-1}; ^{1}H NMR δ=1.03 and 1.17 (9H, 59 : 41, s), 3.45 (0.59×1H, d, *J*=11.0 Hz), 4.51 (0.41×1H, d, *J*=11.0 Hz), 6.02 (0.59×1H, d, *J*=11.0 Hz), 6.29 (0.41×1H, d, *J*=10.1 Hz), 6.5—7.55 (15H, m); ^{13}C NMR δ=28.0 (q, *E*), 28.1 (q, *Z*), 35.5 (s, *E*), 36.0 (s, *Z*), 61.2 (d, *Z*), 61.4 (d, *E*), 125.6 (d), 126.7 (d), 127.2 (d), 127.5 (d), 127.7 (d), 127.9 (d), 128.0 (d), 128.3 (d), 128.7 (d), 128.8 (d), 128.9 (d), 129.2 (d), 129.3 (d), 130.0 (d) , 131.9 (d) , 132.1 (d), 133.7 (d and s, 2C), 134.2 (d), 134.5 (s), 134.6 (s), 134.8 (s), 135.6 (s), 135.7 (d), 135.9 (s), 136.7 (d), 137.0 (s), 139.5 (s); MS *m/z* 390 (M$^+$), 333, 281. Found: *m/z* 281.1361. Calcd for $C_{19}H_{21}S$: M−SPh, 281.1364.

1,3-Bis(ethylthio)-4,4-dimethyl-1-phenyl-1-pentene (*E* : *Z*= 4 : 96, mixture) (Entry 6). IR (neat) 1450, 1370, 1260, 700 cm^{-1}; ^{1}H NMR δ=1.05 (12H, s and t, *J*=7 Hz), 1.30 (3H, t, *J*=7 Hz), 2.37 (2H, q, *J*=7 Hz), 2.53 (2H, m), 3.22 (0.04×1H, d, *J*=11.2 Hz), 4.05 (0.96×1H, d, *J*=10.8 Hz), 5.87 (0.04×1H, d, *J*=11.2 Hz), 5.97 (0.96×1H, d, *J*=10.7 Hz), 7.2—7.4 (3H, m), 7.53 (2H, m); ^{13}C NMR (*Z*-isomer) δ=15.1 (q), 15.4 (q), 24.9 (t), 26.3 (t), 28.0 (q), 35.3 (s), 55.7 (d), 127.7 (d), 128.0 (d), 128.3 (d), 134.8 (d), 136.9 (s), 139.9 (s); MS *m/z* 294 (M$^+$), 237, 233. Found: *m/z* 294.1483. Calcd for $C_{17}H_{26}S_2$: M, 294.1476.

Methyl 4-Phenyl-2,4-bis(phenylthio)-3-butenoate (*E* : *Z*= 25 : 75, mixture) (Entry 7). Pure *Z*-isomer was obtained by recrystallization from ethanol.

***Z*-Isomer:** Mp 74—75 °C; IR (KBr) 1735, 1440, 1325, 1290, 1150, 750, 690 cm^{-1}; ^{1}H NMR δ=3.72 (3H, s), 5.35 (1H, d, *J*=9.8 Hz), 6.39 (1H, d, *J*=9.8 Hz), 6.9—7.1 (5H, m), 7.2 (3H, m), 7.3 (3H, m), 7.4 (2H, m), 7.6 (2H, m); ^{13}C NMR

δ=51.4 (d), 52.7 (q), 126.2 (d), 128.0 (d), 128.2 (d), 128.4 (d), 128.6 (d), 128.7 (d), 129.1 (d), 129.6 (d), 130.5 (d), 132.0 (s), 134.1 (s), 134.6 (d), 138.7 (s), 139.2 (s), 170.3 (s); MS *m/z* 294 (M^+), 237, 233. Found: C, 70.14; H, 5.19; S, 16.23%. Calcd for $C_{23}H_{20}O_2S_2$: C, 70.38; H, 5.14; S, 16.34%.

***E*-Isomer:** ^{1}H NMR δ=3.66 (3H, s), 4.40 (1H, d, *J*=10.7 Hz), 5.75 (1H, d, *J*=10.7 Hz), 6.9—7.6 (15H, m); ^{13}C NMR δ=50.8 (d), 52.5 (q), 122.2 (d), 127.5 (d), 128.0 (d), 128.4 (d), 128.5 (d), 128.9 (d), 129.2 (d), 131.7 (s), 132.3 (s), 133.1 (d), 136.2 (s), 141.9 (s), 170.2 (s).

Methyl 2,4-Bis(ethylthio)-4-phenyl-3-butenoate (*E*:*Z*=25:75, mixture) (Entry 8). IR (neat) 1735, 1450, 1265, 1155, 760, 700 cm^{-1}; ^{1}H NMR δ=1.06 and 1 08 (3H, 75:25, t, *J*=7 Hz), 1.23 and 1.32 (3H, 25:75, t, *J*=7.3 Hz), 2.41 (0.75×2H, q, *J*=7.3 Hz), 2.50 (0.25×2H, m), 2.60 and 2.71 (2H, 25:75, m), 3.74 and 3.77 (3H, 25:75, s), 4.09 (0.25×1H, d, *J*=10.1 Hz), 4.94 (0.75×1H, d, *J*=10.1 Hz), 5.79 (0.25×1H, d, *J*=11.0 Hz), 6.17 (0.75×1H, d, *J*=9.2 Hz), 7.3—7.55 (5H, m); ^{13}C NMR δ=13.8 (q, *E*), 14.4 (q, *E*), 14.7 (q, *Z*), 15.1 (q, *Z*), 25.2 (t, *E*), 25.5 (t, *Z*), 26.1 (t, *E*), 26.5 (t, *Z*), 45.9 (q, *E*), 46.3 (q, *Z*), 52.5 (d, *E*), 52.6 (d, *Z*), 128.1 (d, *Z*), 128.3 (d, *Z*), 128.4 (d and d, 2C, *Z*), 129.2 (d, *E*), 136.8 (s, *E*), 139.0 (s, *Z*), 140.5 (s, *Z*), 141.0 (s, *E*), 171.0 (s, *E*), 171.3 (s, *Z*); MS *m/z* 296 (M^+), 264, 235, 175. Found: *m/z* 296.0911. Calcd for $C_{15}H_{20}O_2S_2$: M, 296.0905.

1,3-Bis(ethylthio)-3-(4-methoxyphenyl)-1-(4-nitrophenyl)-propene (*E*:*Z*=15:85, mixture) (Entry 9). IR (neat) 1595, 1515, 1455, 1345, 1245, 1175, 1110, 1030, 850, 750 cm^{-1}; ^{1}H NMR δ=1.04 and 1.09 (3H, 15:85, t, *J*=7.3 Hz), 1.20 and 1.31 (3H, 15:85, t, *J*=7.3 Hz), 2.29 and 2.41 (2H, 15:85, q, *J*=7 Hz), 2.54 (2H, m), 3.79 (3H, s), 4.42 (0.15×1H, d, *J*=10.7 Hz), 5.43 (0.85×1H, d, *J*=10.3 Hz), 6.16 (0.15×1H, d, *J*=10.8 Hz), 6.37 (0.85×1H, d, *J*=9.8 Hz), 6.88 (2H, d, *J*=8 Hz), 7.23 and 7.35 (2H, 15:85, d, *J*=8 Hz), 7.56 and 7.70 (2H, 15:85, d, *J*=8 Hz), 8.20 and 8.24 (2H, 85:15, d, *J*=8 Hz); ^{13}C NMR (*Z*-isomer) δ=15.0 (q), 15.1 (q), 25.6 (t), 26.7 (t), 47.8 (d), 55.3 (q), 114.2 (d), 123.8 (d), 128.7 (d), 128.9 (d), 132.2 (s), 134.7 (s), 139.0 (d), 146.2 (s), 147.3 (s), 158.9 (s); (*E*-isomer) δ=14.1 (q), 14.5 (q), 25.4 (t), 26.2 (t), 47.3 (d), 55.3 (q), 114.3 (d), 123.6 (d), 128.6 (d), 128.9 (d), 132.2 (s), 134.5 (s), 139.0 (d), 144.4 (s), 147.5 (s), 158.9 (s); MS *m/z* 389 (M^+), 328. Found: *m/z* 328.1015. Calcd for $C_{18}H_{18}NO_3S$: M−SEt, 328.1008.

Methyl 2,4-Bis(phenylthio)-3-pentenoate (*E*:*Z*=38:62, mixture) (Entry 10). IR (neat) 1735, 1477, 1440, 1155, 745, 690 cm^{-1}; ^{1}H NMR δ=1.74 and 1.89 (3H, 38:62, s), 3.67 and 3.69 (3H, 38;62, s), 4.54 (0.38×1H, d, *J*=9.8 Hz), 5.13 (0.62×1H, d, *J*=9.8 Hz), 5.65 (0.38×1H, d, *J*=10.3 Hz), 5.90 (0.62×1H, d, *J*=9.8 Hz), 7.2—7.6 (10H, m); ^{13}C NMR δ=17.4 (q, *E*), 24.0 (q, *Z*), 50.4 (d, *E*), 50.6 (d, *Z*), 52.5 (q, *Z*), 52.6 (q, *E*), 122.7 (d), 126.6 (d), 127.3 (d), 127.8 (d), 128.4 (d), 128.7 (d), 128.9 (d), 129.1 (d), 130.4 (d), 132.1 (s), 132.4 (s), 132.5 (s), 132.7 (d), 132.8 (s), 134.1 (d), 134.7 (d), 136.1 (s), 136.9 (s), 137.2 (d), 170.2 (s, *E*) , 173.8 (s, *Z*); MS *m/z* 330 (M^+), 314, 238, 206. Found: *m/z* 206.0386. Calcd for $C_{11}H_{10}O_2S$: M−SPh−Me, 206.0402.

Reaction of α,β-Unsaturated Ketone Acetals with 1,3-Bis(trimethylsilylthio)propane (Table 7). Reactions were carried out in a manner similar to that described for compounds **8**, using 1.1 equiv of 1,3-bis(trimethylsilylthio)-propane. Analytical data are listed below.

(*E*)-2-Phenyl-2-styryl-1,3-dithiane[14] (Entry 1). IR (KBr) 1595, 1495, 1480, 1445, 1410, 1275, 745, 730, 695 cm^{-1}; ^{1}H NMR δ=1.7—2.2 (2H, m), 2.4—3.2 (4H, m), 6.27 (1H, d, *J*=16 Hz), 6.61 (1H, d, *J*=16 Hz), 6.9—7.4 (8H, m), 7.6—7.8 (2H, m); MS *m/z* 298 (M^+), 223, 191. Found: *m/z* 298.0854. Calcd for $C_{18}H_{18}S_2$: M, 298.0850.

(*E*)-2-*t*-Butyl-2-styryl-1,3-dithiane[15] **and 2-*t*-Butyl-4-phenyl-1,5-dithia-2-cyclooctene** (56:44, mixture) (Entry 2). ^{1}H NMR δ=1.18 (0.56×9H, s), 1.22 (0.44×9H, s), 1.7—2.2 (2H, m), 2.5—3.0 (4H, m), 5.62 (0.44×1H, d, *J*=10 Hz), 6.14 (0.44×1H, d, *J*=10 Hz), 6.35 (0.56×1H, d, *J*=16 Hz), 6.80 (0.56×1H, d, *J*=16 Hz), 7.2—7.5 (5H, m); ^{13}C NMR δ=25.3 (t), 26.0 (q), 27.3 (t), 29.5 (q), 30.3 (t), 35.2 (t), 37.1 (t), 40.0 (s), 40.3 (s), 48.0 (d), 65.7 (s), 126.5 (d), 127.4 (d), 127.7 (d), 128.0 (d), 128.6 (d), 131.4 (d), 133.0 (d), 135.2 (d), 136.7 (s), 140.1 (s), 145.5 (s).

(*E*)-2-(3,3-Dimethyl-1-butenyl)-2-phenyl-1,3-dithiane and 4-*t*-Butyl-2-phenyl-1,5-dithia-2-cyclooctene (43:57, mixture) (Entry 3). ^{1}H NMR δ=1.09 (9H, s), 1.9—2.1 (2H, m), 2.4—3.0 (4H, m), 4.53 (0.57×1H, d, *J*=11 Hz), 5.61 (0.43×1H, d, *J*=16 Hz), 5.84 (0.43×1H, d, *J*=16 Hz), 6.43 (0.57×1H, d, *J*=11 Hz), 7.2—7.4 (3H, m), 7.68 (0.57×2H, m), 7.77 (0.43×2H, m); ^{13}C NMR δ=24.7 (t), 28.1 (q), 28.6 (t), 29.3 (t), 29.8 (q), 33.3 (s), 33.9 (s), 34.9 (t), 35.2 (t), 56.3 (d), 58.6 (s), 127.0 (d), 127.7 (d), 127.8 (d), 128.3 (d and d, 2C), 128.5 (d), 134.3 (s), 136.5 (d), 140.8 (s), 142.0 (s), 146.6 (d).

Reactions of 11 with Silylated Nucleophiles (Table 8). The following is a typical reaction procedure for (*Z*)-4,4-dimethyl-1-phenyl-1,3-bis(phenylthio)-2-pentene (**11**) (R^1=^{t}Bu, R^2=Ph) with the trimethylsilyl enol ether of *t*-butyl methyl ketone (Entry 1): In an argon atmosphere, **11** (R^1=^{t}Bu, R^2=Ph) (52.3 mg, 0.134 mmol) and the trimethylsilyl enol ether of *t*-butyl methyl ketone (39.6 mg, 0.230 mmol) were dissolved in CH_2Cl_2 (2 ml), to which was added 1.0 M $SnCl_4$ solution in CH_2Cl_2 (0.15 ml, 0.15 mmol) at 0 °C. The reaction mixture was stirred for 1 h at 0 °C and quenched with aqueous $NaHCO_3$ solution. The organic materials were extracted with CH_2Cl_2 and the combined extract was dried over Na_2SO_4. After evaporation of the solvent, the residue was purified by preparative TLC (silica gel, hexane:AcOEt=96:4) to afford (*Z*)-2,2,8,8-tetramethyl-5-phenyl-7-phenylthio-6-nonen-3-one (42.7 mg, 0.112 mmol, 84%). IR (neat) 1710, 1580, 1480, 1365, 1070, 740, 700 cm^{-1}; ^{1}H NMR δ=0.98 (9H, s), 1.15 (9H, s), 2.65 (1H, dd, *J*=17 Hz, 6 Hz), 2.95 (1H, dd, *J*=17 Hz, 8 Hz), 4.43 (1H, m), 6.36 (1H, d, *J*=9 Hz), 7.0—7.3 (10H, m); MS *m/z* 380 (M^+), 281, 271. Found: *m/z* 380.2170. Calcd for $C_{25}H_{32}OS$: M, 380.2174.

Other analytical data follow.

(*Z*)-6,6-Dimethyl-1,3-diphenyl-5-phenylthio-4-hepten-1-one (Entry 2). IR (neat) 1705, 1495, 1480, 1440, 1070, 755, 740, 700 cm^{-1}; ^{1}H NMR δ=1.08 (9H, s), 2.95 (1H, dd, *J*=17 Hz, 8 Hz), 3.10 (1H, dd, *J*=17 Hz, 7 Hz), 4.85 (1H, m), 6.42 (1H, d, *J*=10 Hz), 6.95—7.5 (15H, m); MS *m/z* 400 (M^+), 301, 291. Found: *m/z* 400.1850. Calcd for $C_{27}H_{28}OS$: M, 400.1861.

(*Z*)-4,4-Dimethyl-1-phenyl-3-phenylthio-2-pentene (Entry 3). IR (neat) 1580, 1480, 1455, 1440, 1025, 735, 700 cm^{-1}; ^{1}H NMR δ=1.20 (9H, s), 3.54 (2H, d, *J*=7 Hz), 6.33 (1H, t, *J*=7 Hz), 7.0—7.5 (10H, m); MS *m/z* 282 (M^+), 255. Found: *m/z* 282.1433. Calcd for $C_{19}H_{22}S$: M, 282.1442.

(*Z*)-7,7-Dimethyl-4-phenyl-6-phenylthio-1,5-octadiene (Entry 4). IR (neat) 1640, 1580, 1480, 1440, 735, 700 cm^{-1}; ^{1}H NMR δ=1.19 (9H, s), 2.41 (2H, m), 3.95 (1H, m), 4.92 (2H, m), 5.61 (1H, m), 6.35 (1H, d, *J*=10 Hz), 7.0—7.6 (10H, m); MS *m/z* 322 (M^+), 281, 171. Found: *m/z* 322.1728. Calcd for $C_{22}H_{26}S$: M, 322.1755.

(Z)-2,2-Dimethyl-5,7-diphenyl-7-phenylthio-6-hepten-3-one (Entry 5). IR (neat) 1710, 1490, 1480, 1455, 1070, 760, 740, 700 cm^{-1}; ^1H NMR δ=1.07 (9H, s), 2.89 (1H, dd, J=17 Hz, 7 Hz), 3.13 (1H, dd, J=17 Hz, 7 Hz), 4.85 (1H, m), 6.42 (1H, d, J=9 Hz), 7.0—7.5 (15H, m); MS m/z 400 (M^+), 301, 291. Found: m/z 400.1884. Calcd for $C_{27}H_{28}OS$: M, 400.1861.

1,3,5-Triphenyl-5-phenylthio-4-penten-1-one (mixture of E,Z-isomer, 34:66) (Entry 6). IR (neat) 1685, 1600, 1580, 1490, 1480, 1450, 740, 700 cm^{-1}; ^1H NMR δ=3.29 (0.34×2H, d, J=7 Hz), 3.46 (0.66×1H, dd, J=16 Hz, 8 Hz), 3.56 (0.66×1H, dd, J=16 Hz, 7 Hz), 4.20 (0.34×1H, dt, J=10 Hz, 7 Hz), 5.01 (0.66×1H, m), 6.16 (0.34×1H, d, J=11 Hz), 6.48 (0.66×1H, d, J=10 Hz), 6.9—8.0 (20H, m); MS m/z 420 (M^+), 311, 301. Found: m/z 420.1541. Calcd for $C_{29}H_{24}OS$: M, 420.1548.

(Z)-1,3-Diphenyl-1-phenylthio-1-propene (Entry 7). IR (neat) 1580, 1490, 1480, 1455, 1025, 760, 740, 695 cm^{-1}; ^1H NMR δ=3.91 (2H, d, J=7 Hz), 6.55 (1H, t, J=7 Hz), 7.0—7.6 (15H, m); MS m/z 302 (M^+), 218, 193. Found: m/z 302.1125. Calcd for $C_{21}H_{18}S$: M, 302.1129.

Methyl (Z)-4-Phenyl-2-phenacyl-4-phenylthio-3-butenoate (Entry 8). IR (neat) 1735, 1685, 1450, 1215, 740, 690 cm^{-1}; ^1H NMR δ=3.35 (1H, dd, J=18 Hz, 6 Hz), 3.68 (1H, dd, J=18 Hz, 7 Hz), 3.74 (3H, s), 4.62 (1H, m), 6.46 (1H, d, J=9 Hz), 7.0—8.0 (15H, m); MS m/z 402 (M^+), 370, 293, 261. Found: m/z 402.1281. Calcd for $C_{25}H_{22}O_3S$: M, 402.1290.

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