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Oxidative Generation of Thioalkyl Cations from 2-Tributylstannyl-1,3-dithianes and 1-(Tributylstannyl)alkyl Sulfides and Their Reactions with Olefinic Nucleophiles

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2-Tributylstannyl-1,3-dithianes and 1-(tributylstannyl)alkyl sulfides are oxidized with ammonium hexanitratocerate(IV) or ferrocenium hexafluorophosphate to generate their cation radicals, which dissociate into the carbocations and tributylstannyl radical. The carbocations thus generated react with olefinic nucleophiles to afford the corresponding addition products in good yield.

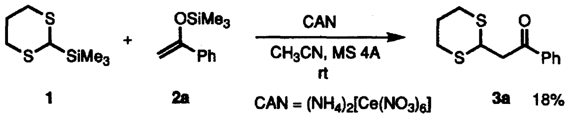
Sulfides are easily oxidized to generate their cation radicals, and, in terms of synthetic chemistry, these active species have mainly been used for the transformation to sulfoxides[1] or the formation of sulfonium salts.[2,3] For construction of carbon skeletons, however, the cation radicals of sulfides have found quite a limited application: Only cation radicals of vinyl sulfides were used as dienophiles in the Diels–Alder reaction.[4]

In the previous paper,[5] we reported that allylic phenyl sulfides react with silyl enol ethers by the oxidation with ammonium hexanitratocerate(IV) (CAN) to afford α-phenylthio β,γ-unsaturated ketones. In these reactions, silyl enol ethers initially attack nucleophilically the sulfur of the cation radicals of allylic sulfides, and the carbon–carbon bond formation is accomplished by the successive [2,3]-Wittig rearrangement of the sulfonium salts thus generated. As shown in this example, cation radicals of sulfides are easily generated by the one-electron oxidation, but they generally react with nucleophiles on the sulfur atoms.[1—3,5] If cation radicals of sulfides could be readily transformed to reactive species such as carbocations or carbon radicals, carbon–carbon bond formation would be directly achieved via cation radicals of sulfides. The examples of the conversion of cation radicals to carbon reactive species have been known in the photochemical reactions of some silyl compounds. Mizuno et al. reported that the reactions of allylsilanes with dicyanoethenes or aromatic nitriles proceeded by photo irradiation to afford intermolecular addition products,[6] and Mariano et al. reported that a diethyl(silylmethyl)amine reacts with α,β-unsaturated ketones to give the corresponding adducts under similar conditions.[7] In these reactions, allyl radicals and aminomethyl radicals are formed by the elimination of cationic silyl groups from the cation radicals which are generated from these organosilanes by single-electron transfer to the dicyanoethenes or unsaturated ketones. We expected that a cation radical of a 1,3-dithiane having a silyl group at 2-position also dissociates in a similar manner into a cationic silyl group and a 1,3-dithian-2-yl radical, which could be used as a reactive intermediate for constructing carbon skeletons.

Results and Discussion

Reactions of 2-Tributylstannyl-1,3-dithianes with Olefinic Nucleophiles.[8]

The reaction of 2-trimethylsilyl-1,3-dithiane (**1**) and α-trimethylsiloxystyrene (**2a**) was examined by using CAN as an oxidizing agent, with the expectation that trimethylsilyl cation[9] would be eliminated from the cation radical of **1** to produce 1,3-dithian-2-yl radical, which would be trapped by the silyl enol ether **2a**. When the dithiane **1** was treated with 2.1 molar amounts of CAN in the presence of 2.1 molar amounts of **2a**, the desired addition product **3a** was obtained but only in 18% yield (Eq. 1).

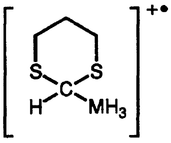


(1)

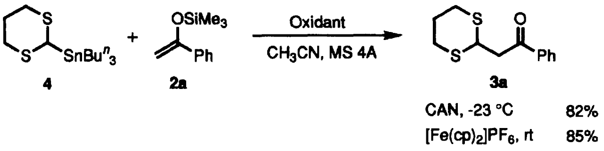
The low yield of **3a** suggested that the cleavage of the carbon–silicon bond did not proceed smoothly in the cation radical of **1** and the cation radical was attacked by nucleophiles such as a nitrate ion, **2a**, and a trace of water, etc. In search of a suitable substituent which is eliminated more easily than trimethylsilyl group, semiempirical molecular orbital calculation was performed by MOPAC ver. 6.01 using PM3 Hamiltonian on cation radicals of 2-silyl, 2-germyl, and 2-stannyl-1,3-dithianes to compare two-center energies of their carbon–metal bonds.[10] By the calculation, the carbon–metal bonds in these cation radicals become weaker in the order of silyl, germyl, and stannyl derivatives as listed in Table 1.

Based on the above estimation, 2-tributylstannyl-1,3-dithiane (**4**) was prepared, and the reaction of **4** with 2.1 molar amounts of the silyl enol ether **2a** was tried in acetonitrile using 2.1 molar amounts of CAN. The reaction proceeded at −23 °C and the yield of the product **3a** was improved to 82% (Eq. 2).

Table 1. MO Calculation of the Cation Radicals



M	Two center energy (C–M)/eV
Si	−12.5
Ge	−10.8
Sn	−9.3



(2)

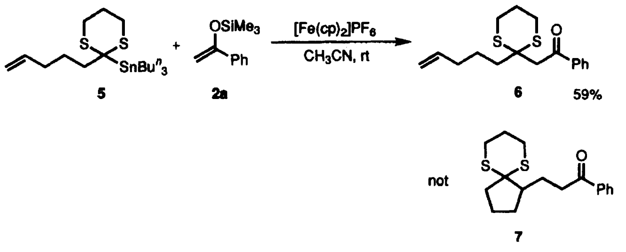
The reaction conditions were optimized on the effects of oxidants, solvents, and reaction temperature. Concerning the amount of oxidant, the use of two molar amounts of CAN is indispensable but sufficient to complete the reaction. Ferrocenium hexafluorophosphate ($[Fe(cp)_2]PF_6$, cp=η^5-cyclopentadienyl) was also found to be an effective oxidizing agent in the above reaction.

The reaction proceeded smoothly and in high yield in acetonitrile, whereas the reaction was somewhat slow and the yield was not so high in other solvents such as dimethylformamide (DMF), nitromethane, and dichloromethane. At low temperature (−78 °C), the oxidation with CAN proceeded very slowly and **4** was recovered (54%) along with a small amount (11%) of the product **3a**.[11]

Under the optimum reaction conditions (CAN, CH_3CN, −23 °C, or $[Fe(cp)_2]PF_6$, CH_3CN, r.t.), reactions of the 2-stannyl-1,3-dithiane **4** with various olefinic compounds were carried out and the results are shown in Table 2. Generally, silyl enol ethers reacted with **4** to give the addition products by using either of the oxidizing reagents. For reactions with a ketene silyl acetal **2e**, allyltriphenylstannane (**2f**), allyltrimethylsilane (**2g**), and α-methylstyrene (**2h**), the use of $[Fe(cp)_2]PF_6$ was required to obtain the products in good yield. Although olefins **2e**—**2g** have low oxidation potentials,[12] the possibility that these olefins (**2e**—**2g**) were consumed by the oxidation with CAN is excluded, since the oxidation of the olefins hardly proceeded at −23 °C. Presumably, when CAN was employed as an oxidant, nitrate ion attacked the cationic intermediates competitively with these olefinic nucleophiles.

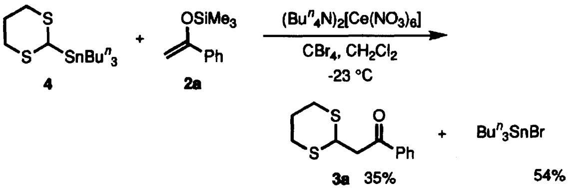
Two modes are possible for the cleavage of the carbon–tin bond of the cation radical **A** as depicted in Scheme 1. One is the route in which tributylstannyl cation may be eliminated from the cation radical **A** to generate a carbon radical **B**. In the other route, **A** may dissociate into tributylstannyl radical and 1,3-dithian-2-yl cation **C**.

On the analogy with the cleavage of the cation radicals of allylsilane and diethyl(silylmethyl)amine mentioned before,[6,7] we had though in the early stage that the radical intermediate **B** might be generated. The trapping of the radical species **B** was tried by using radical scavengers such as 2,2,6,6-tetramethyl-1-piperidinyloxyl radical and *t*-butyl isocyanide, or by using hydrogen donors such as 1,4-cyclohexadiene and 2,4-di-*t*-butyl-4-methylphenol, but these attempts resulted in failure. The intramolecular cyclization was also examined to trap 1,3-dithian-2-yl radical by employing **5**, but only the adduct **6** with the silyl enol ether was isolated (Eq. 3). These results confirmed that 1,3-dithian-2-yl radical (**B**) was not formed by the oxidation of the 2-stannyl-1,3-dithiane **4**.



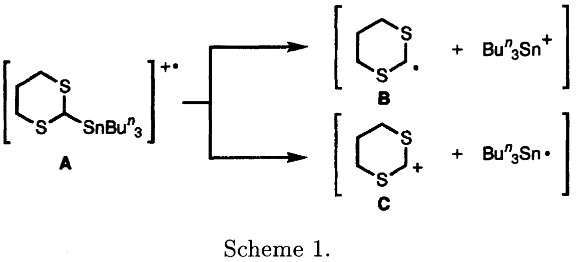
(3)

Accordingly, the reaction was considered to proceed via 1,3-dithian-2-yl cation **C** and the trapping of tributylstannyl radical was then examined. When a mixture of **4** and **2a** was treated with CAN in the presence of carbon tetrabromide which is known as an efficient radical trapping agent,[13] bromotributylstannane was isolated in 54% yield along with the addition product **3a** (Eq. 4).

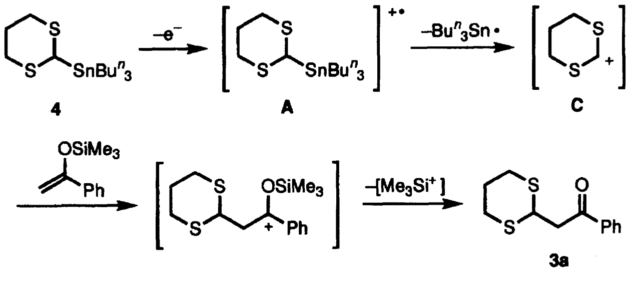


(4)

The formation of bromotributylstannane confirms that the stannyl radical is eliminated from the cation radical **A** to generate the carbocation **C**, which reacts with olefinic nucleophiles as shown in Scheme 2. Totally, two molar amounts of the oxidizing agent are consumed

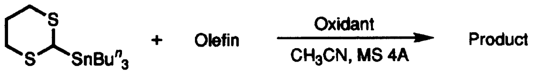


Scheme 1.

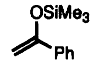
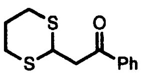
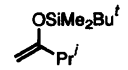
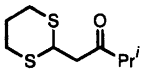
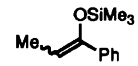
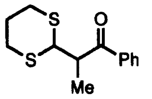
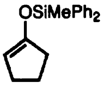
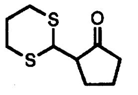
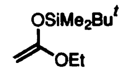
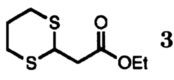
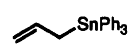
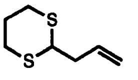
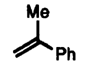
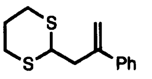


Scheme 2.

Table 2. Reactions of 2-Tributylstannyl-1,3-dithiane (4) with Olefins



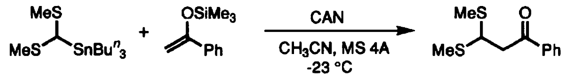
4

Olefin		Oxidant	Temp/°C	Product		Yield/%
	2a	CAN	−23		3a	82
		$[\mathrm{Fe(cp)_2}]\mathrm{PF_6}$	r.t.			85
	2b	CAN	−23		3b	87
		$[\mathrm{Fe(cp)_2}]\mathrm{PF_6}$	r.t.			61
	2c	CAN	−23		3c	85
		$[\mathrm{Fe(cp)_2}]\mathrm{PF_6}$	r.t.			78
	2d	CAN	−23		3d	85
		$[\mathrm{Fe(cp)_2}]\mathrm{PF_6}$	r.t.			74
	2e	CAN	−23		3e	25
		$[\mathrm{Fe(cp)_2}]\mathrm{PF_6}$	r.t.			54
	2f	CAN	−23		3f	27
		$[\mathrm{Fe(cp)_2}]\mathrm{PF_6}$	r.t.			67
	2g	$[\mathrm{Fe(cp)_2}]\mathrm{PF_6}$	r.t.		3f	66
	2h	$[\mathrm{Fe(cp)_2}]\mathrm{PF_6}$	r.t.		3h	75

for the one-electron oxidation of 4 and for the conversion of tributylstannyl radical to the stannyl cation, respectively.

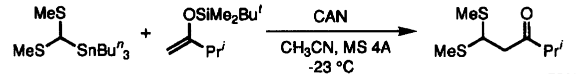
2-Methyl- and 2-phenyl-2-tributylstannyl-1,3-dithianes (**8** and **10**) also reacted with olefinic nucleophiles as shown in Table 3. They afforded moderate to good yield of products in the reactions with an aromatic silyl enol ether **2a** and a cyclic silyl enol ether **2i**, but the reactivity toward and aliphatic silyl enol ether **2b** is rather poor as compared with that of the non-substituted 2-stannyl-1,3-dithiane **4**.

In addition to the 1,3-dithiane derivatives **4**, **8**, and **10**, the reaction also proceeded by employing a stannylated bis(methylthio)methane **12** and a 1,3-benzodithiole derivative **14**, but the yields were somewhat poorer as compared with the 1,3-dithiane derivatives (Eqs. 5, 6, 7, and 8).



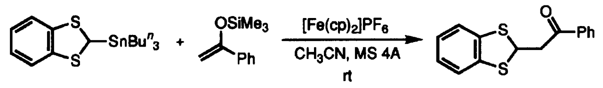
12 2a 13a 82%

(5)



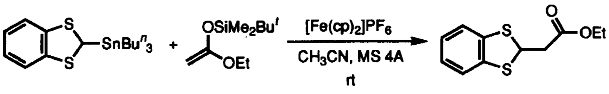
12 2b 13b 53%

(6)



14 2a 15a 92%

(7)

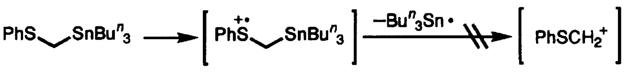


14 2e 15e 56%

(8)

Reactions of 1-(Tributylstannyl)alkyl Sulfides with Olefinic Nucleophiles. The reaction of phenyl tributylstannylmethyl sulfide (**16**) with the silyl enol ether **2a** gave no addition product. Since **16** was consumed completely by the oxidation, the conversion of the cation radical **D** to the carbocation **E** seemed not to proceed smoothly because of the poorer stability of the cation intermediate **E** in comparison to 1,3-dithian-2-yl cation (Scheme 3).

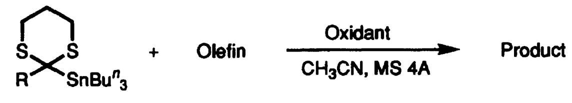
In contrast, the addition reaction of benzylic sulfides, phenyl α-tributylstannylbenzyl sulfide (**17**) and methyl α-tributylstannylbenzyl sulfide (**19**) proceeded smoothly and the products **18** and **20** were obtained



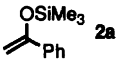
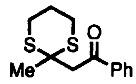
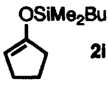
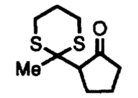
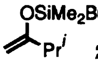
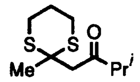
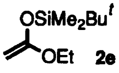
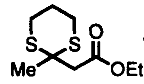
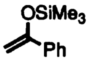
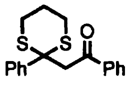
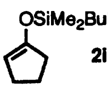
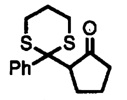
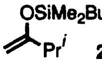
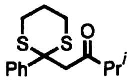
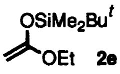
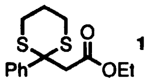
16 D E

Scheme 3.

Table 3. Reactions of 2-Substituted-2-tributylstannyl-1,3-dithiane (**8** and **10**) with Olefins



8: R = Me, **10**: R = Ph

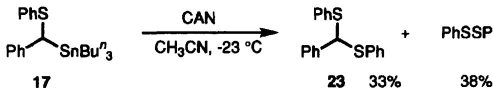
Olefin	Oxidant	Temp/°C	Product	Yield/%
8:R=Me				
 **2a**	CAN	−23	 **9a**	29
	[Fe(cp)$_2$]PF$_6$	r.t.		64
 **2i**	[Fe(cp)$_2$]PF$_6$	r.t.	 **9i**	74
 **2b**	[Fe(cp)$_2$]PF$_6$	r.t.	 **9b**	22
 **2e**	[Fe(cp)$_2$]PF$_6$	r.t.	 **9e**	23
10:R=Ph				
 **2a**	CAN	−23	 **11a**	0$^{a)}$
	[Fe(cp)$_2$]PF$_6$	r.t.		92
 **2i**	[Fe(cp)$_2$]PF$_6$	r.t.	 **11i**	78
 **2b**	[Fe(cp)$_2$]PF$_6$	r.t.	 **11b**	28
 **2e**	[Fe(cp)$_2$]PF$_6$	r.t.	 **11e**	22

a) Complex mixture.

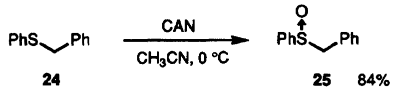
in 83 and 90% yield, respectively. In Table 4 is summarized the results of the reactions of **17** and **19** with various olefins. When silyl enol ethers were used, the corresponding addition products were obtained in excellent yield. Allyltrimethylsilane (**2g**) and allyltriphenylstannane (**2f**) also afforded the addition products.

Phenyl group on the carbon adjacent to the sulfur atom (compounds **17** and **19**) is not essential for the formation of cationic intermediate. A 1-(tributylstannyl)alkyl sulfide such as **21** was also converted to the cationic intermediate by the oxidation, however, the use of [Fe(cp)$_2$]PF$_6$ is required to obtain the addition products in good yield (Table 5).

Thus the 2-tributylstannyl-1,3-dithianes and 1-(tributylstannyl)alkyl sulfides are easily oxidized with CAN or [Fe(cp)$_2$]PF$_6$ and the corresponding carbocations are generated with the elimination of tributylstannyl radical. Tributylstannyl substituent is indispensable for the generation of carbocations of sulfides. That is, the oxidation of the α-tributylstannylbenzyl sulfide **17** with CAN in the absence of olefinic nucleophiles afforded diphenyl disulfide and/or benzaldehyde diphenyldithioacetal (**23**) through the benzyl cation, whereas the oxidation of benzyl phenyl sulfide (**24**) in the same manner gave the sulfoxide **25** exclusively, apparently indicating that the formation of the carbocation does not occur from the cation radical of **24** (Eqs. 9 and 10).



(9)



(10)

Furthermore, the introduction of tributylstannyl group contributes in facilitating the oxidation of sulfides. 2-Tributylstannyl-1,3-dithiane has considerably lower oxidation potential than 1,3-dithiane itself. The oxidation potentials (E_{ox}) of α-stannylated sulfides synthesized here were measured in acetonitrile and compared with those of non-substituted ones. For example,

Table 4. Reactions of α-Stannylbenzyl Sulfides (**17** and **19**) with Olefins

17: R = Ph, **19**: R = Me

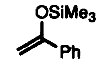
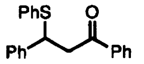
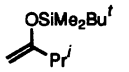
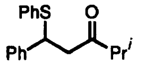
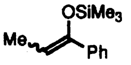
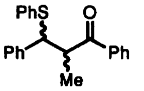
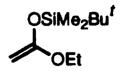
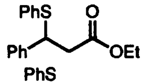
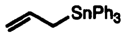
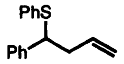
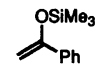
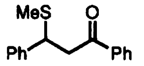
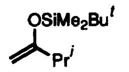
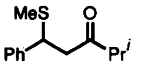
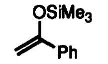
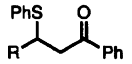
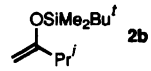
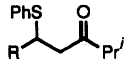
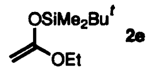
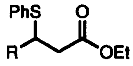
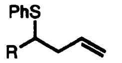
Olefin	Oxidant	Temp/°C	Product	Yield/%
17:R=Ph				
 **2a**	CAN $[\mathrm{Fe(cp)_2}]\mathrm{PF_6}$	0 r.t.	 **18a**	83 88
 **2b**	CAN $[\mathrm{Fe(cp)_2}]\mathrm{PF_6}$	−23 r.t.	 **18b**	90 84
 **2c**	CAN $[\mathrm{Fe(cp)_2}]\mathrm{PF_6}$	−23 r.t.	 **18c**	89 96
 **2e**	CAN $[\mathrm{Fe(cp)_2}]\mathrm{PF_6}$	r.t. r.t.	 **18e**	31 48
 **2f**	$[\mathrm{Fe(cp)_2}]\mathrm{PF_6}$	r.t.	 **18f**	84
 **2g**	CAN $[\mathrm{Fe(cp)_2}]\mathrm{PF_6}$	0 r.t.	**18f** **18f**	16 59
19:R=Me				
 **2a**	CAN $[\mathrm{Fe(cp)_2}]\mathrm{PF_6}$	−23 r.t.	 **20a**	90 86
 **2b**	CAN $[\mathrm{Fe(cp)_2}]\mathrm{PF_6}$	−23 r.t.	 **20b**	95 83

Table 5. Reactions of Sulfide **21** with Olefins

21

Olefin	Oxidant	Temp/°C	Product[a)]	Yield/%
 **2a**	CAN $[\mathrm{Fe(cp)_2}]\mathrm{PF_6}$	0 r.t.	 **22a**	76 85
 **2b**	CAN $[\mathrm{Fe(cp)_2}]\mathrm{PF_6}$	0 r.t.	 **22b**	8 82
 **2e**	CAN $[\mathrm{Fe(cp)_2}]\mathrm{PF_6}$	0 r.t.	 **22e**	7 36
 **2g**	$[\mathrm{Fe(cp)_2}]\mathrm{PF_6}$	r.t.	 **22g**	26

a) R=$\mathrm{PhCH_2CH_2}$.

E_{ox} value of 1,3-dithiane was 0.8 V higher than that of 2-tributylstannyl-1,3-dithiane (**4**), and E_{ox} value of benzyl phenyl sulfide (**24**) was 0.6 V higher than that of phenyl α-tributylstannylbenzyl sulfide (**17**). These measurements show that the oxidation potentials are lowered by introducing tributylstannyl group at α-position of the sulfides. This tendency is in accordance with the recent reports by Yoshida et al.[14] and Glass et al.;[15] 1-hetero atom substituted alkyl stannanes (and also silanes, germanes) exhibit lower oxidation potentials than non-substituted stannanes. Yoshida et al. also recently reported that the anode oxidation of these substrates in the presence of allyltrimethylsilane affords allylated products via the corresponding carbocation intermediates.[16]

In conclusion, 2-tributylstannyl-1,3-dithianes and 1-(tributylstannyl)alkyl sulfides react with olefinic nucleophiles by the oxidation with CAN or $[\mathrm{Fe(cp)_2}]\mathrm{PF_6}$, giving intermolecular addition products. Especially by employing 1,3-dithiane derivatives, this method enables the introduction of masked formyl and acyl moieties to olefinic nucleophiles under mild reaction conditions.

Experimental

General. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were recorded on a Bruker AM 500 spectrometer in $CDCl_3$ solutions, using tetramethylsilane as an internal standard. IR spectra were recorded on a Horiba FT 300-S spectrophotometer. High-resolution mass spectra were obtained with JEOL JMS-D300 and JMS-SX102A mass spectrometer at ionization energy of 70 eV. Melting points were uncorrected.

Cyclic voltammetry was carried out with a Hokuto Denko HA-151 potentiostat/galvanostat connected to a Hokuto Denko HA-111 function generator with Riken Denshi F-35 X-Y recorder. We used an undivided cell equipped with platinum disk anode and a platinum wire cathode in 0.1 mol dm^{-3} Et_4NClO_4/CH_3CN. Ag/AgI (saturated NaI solution in CH_3CN) electrode was used as the reference. The sweep rate was 100 mV s^{-1}.

Acetonitrile, propionitrile, and dichloromethane were distilled from P_2O_5, then CaH_2, and dried over Molecular Sieves 4A (MS 4A). DMF was dried over P_2O_5, then distilled from CaH_2, and stored under argon atmosphere over MS 4A. CAN (Kanto Chemical Co., Inc., guaranteed grade) was dried under vacuum at 80 °C before use. $(Bu^n_4N)_2[Ce(NO_3)_6]$ (TBACN) was prepared according to the literature,[17] and dried by the same manner. $[Fe(cp)_2]PF_6$ was prepared by the known method.[18] Silyl enol ethers (**2a**—**2e**, **2i**),[19] allyltriphenylstannane (**2f**),[20] and allyltrimethylsilane (**2g**)[21] were synthesized according to the literature procedures.

Reactions were monitored by thin-layer chromatography (TLC) using pre-coated silica-gel plates (Merck Kieselgel 60 F-254 Art.5715). Silica-gel column chromatography was carried out with Merck Kieselgel 60 Art.7734. Preparative TLC was performed on a silica-gel (Wakogel B-5F).

All reactions were carried out under an argon atmosphere.

Preparation of Tributylstannyl Dithioacetals. 2-Tributylstannyl-1,3-dithiane (**4**),[22] 2-methyl-2-tributylstannyl-1,3-dithiane (**8**),[22] and [bis(methylthio)methyl]tributylstannane (**12**)[23] were prepared according to the literature. Other stannyl dithioacetals were synthesized in the same manner and purified by silica-gel column chromatography. Spectral data and physical properties of the new compounds are as follows.

2-(4-Pentenyl)-2-tributylstannyl-1,3-dithiane (5). Colorless oil; IR (neat) 3076, 2929, 1639 cm^{-1}; ^{1}H NMR δ=0.88 (9H, t, J=7.3 Hz), 0.96—1.10 (6H, m), 1.29—1.36 (6H, m), 1.45—1.60 (8H, m), 2.01—2.08 (2H, m), 2.12—2.15 (2H, m), 2.20—2.24 (2H, m), 2.35—2.38 (2H, m), 3.10—3.13 (2H, m), 4.95—5.05 (2H, m), 5.75—5.87 (1H, m). Found: C, 52.68; H, 8.58; S, 13.59%. Calcd for $C_{21}H_{42}S_2Sn$: C, 52.83; H, 8.87; S, 13.43%.

2-Phenyl-2-tributylstannyl-1,3-dithiane (10). Colorless oil; IR (neat) 3053, 2922, 1462, 773, 700 cm^{-1}; ^{1}H NMR δ=0.83 (9H, t, J=7.3 Hz), 0.86—0.99 (6H, m), 1.19—1.27 (6H, m), 1.32—1.42 (6H, m), 1.86—1.91 (1H, m), 2.12—2.20 (1H, m), 2.23—2.28 (2H, m), 2.82—2.89 (2H, m), 7.06—7.09 (1H, m), 7.30—7.33 (2H, m), 7.87—7.90 (2H, m). Found: C, 54.28; H, 7.73; S, 13.41%. Calcd for $C_{22}H_{38}S_2Sn$: C, 54.44; H, 7.89; S, 13.21%.

2-Tributylstannyl-1,3-benzodithiole (14).[24] Colorless oil; IR (neat) 3057, 2954, 1439, 714 cm^{-1}; ^{1}H NMR δ=0.90 (9H, t, J=7.3 Hz), 1.09—1.13 (6H, m), 1.31—1.35 (6H, m), 1.50—1.60 (6H, m), 4.39 (1H, s), 6.95—6.97 (2H, m), 7.21—7.23 (2H, m). HRMS Found: m/z 444.0983. Calcd for $C_{19}H_{32}S_2Sn$: M, 444.0969.

Typical Procedure for the Reaction of 2-Tributylstannyl-1,3-dithiane with Olefinic Nucleophiles. To an acetonitrile solution (2 ml) of CAN (231.7 mg, 0.423 mmol) including suspended MS 4A[25] (0.2 g) was added an acetonitrile solution (2 ml) of 2-tributylstannyl-1,3-dithiane (**4**) (81.2 mg, 0.198 mmol) and the silyl enol ether **2a** (73.1 mg, 0.380 mmol) at −23 °C. After being stirred for 20 min, the reaction was quenched with saturated aq $NaHCO_3$. Insoluble materials were removed by filtration through a celite pad, which was washed several times with dichloromethane. The organic phase was separated and the aqueous phase was extracted with dichloromethane three times. The combined organic extracts were dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure. The residue was purified by TLC (hexane–ethyl acetate, 7:1) to afford the product **3a** (38.7 mg, 0.162 mmol, 82%).

The reaction with $[Fe(cp)_2]PF_6$ was performed in a similar manner, except for the reaction temperature (r.t.) and the reaction time (1—2 h).

Spectral data and physical properties of the products are as follows.

2-Phenacyl-1,3-dithiane (3a). Colorless crystals; mp 59.5—60.0 °C (hexane–ethyl acetate); IR (KBr) 2902, 1691, 764, 692 cm^{-1}; ^{1}H NMR δ=1.83—1.93 (1H, m), 2.10—2.15 (1H, m), 2.83—2.89 (2H, m), 2.97—3.01 (2H, m), 3.36 (2H, d, J=6.8 Hz), 4.76 (1H, t, J=6.8 Hz), 7.46—7.49 (2H, m), 7.56—7.60 (1H, m), 7.95—7.97 (2H, m). Found: C, 60.45; H, 5.93; S, 26.65%. Calcd for $C_{12}H_{14}OS_2$: C, 60.46; H, 5.92; S, 26.90%.

2-(3-Methyl-2-oxobutyl)-1,3-dithiane (3b). Colorless crystals; mp 49.0—50.0 °C (petroleum ether); IR (KBr) 2966, 1714 cm^{-1}; ^{1}H NMR δ=1.12 (6H, d, J=6.9 Hz), 1.80—1.90 (1H, m), 2.08—2.15 (1H, m), 2.60 (1H, sept, J=6.9 Hz), 2.81—2.85 (2H, m), 2.83 (2H, d, J=6.9 Hz), 2.91—2.98 (2H, m), 4.53 (1H, t, J=6.9 Hz). Found: C, 52.86; H, 7.78; S, 31.28%. Calcd for $C_9H_{16}OS_2$: C, 52.90; H, 7.89; S, 31.38%.

2-(1-Benzoylethyl)-1,3-dithiane (3c). Colorless oil; IR (neat) 2935, 2900, 1678, 760, 710 cm^{-1}; ^{1}H NMR δ=1.33 (3H, d, J=6.9 Hz), 1.81—1.91 (1H, m), 2.02—2.09 (1H, m), 2.75—2.91 (4H, m), 3.89 (1H, dq, J_d=8.9, J_q=6.9 Hz), 4.41 (1H, d, J=8.9 Hz), 7.42—7.47 (2H, m), 7.54—7.58 (1H, m), 7.94—7.96 (2H, m). HRMS Found: m/z 252.0653. Calcd for $C_{13}H_{16}OS_2$: M, 252.0644.

2-(2-Oxocyclopentyl)-1,3-dithiane (3d).[26] Colorless crystals; mp 75.0—75.5 °C (hexane–ethyl acetate); IR (KBr) 2912, 1738, 1267 cm^{-1}; ^{1}H NMR δ=1.71—1.87 (2H, m), 2.01—2.17 (4H, m), 2.22—2.29 (1H, m), 2.32—2.39 (1H, m), 2.44—2.48 (1H, m), 2.80—2.87 (2H, m), 2.93—3.06 (2H, m), 4.63 (1H, d, J=3.4 Hz); ^{13}C NMR δ=20.49, 25.33, 25.53, 30.61, 31.39, 38.59, 48.05, 53.35, 216.33.

Ethyl 1,3-Dithiane-2-acetate (3e). Colorless oil; IR (neat) 2937, 2902, 1735, 1227, 1147 cm^{-1}; ^{1}H NMR δ=1.28 (3H, t, J=7.1 Hz), 1.88—1.95 (1H, m), 2.09—2.15 (1H, m), 2.77 (2H, d, J=7.4 Hz), 2.67—2.90 (4H, m), 4.18 (2H, q, J=7.1 Hz), 4.41 (1H, t, J=7.4 Hz). HRMS Found: m/z 206.0433. Calcd for $C_8H_{14}O_2S_2$: M, 206.0436.

2-Allyl-1,3-dithiane (3f).[27] Colorless oil; IR (neat) 2897, 1639 cm^{-1}; ^{1}H NMR δ=1.81—1.90 (1H, m), 2.09—2.15 (1H, m), 2.51 (2H, t-like dd), 2.81—2.92 (4H, m), 4.10 (1H, t, J=6.9 Hz), 5.12—5.18 (2H, m), 5.83—5.90 (1H, m).

2-(2-Phenylallyl)-1,3-dithiane (3h). Colorless oil; IR (neat) 3082, 2897, 1628, 904, 781, 706 cm^{-1}; ^{1}H NMR δ=1.78—1.86 (1H, m), 2.04—2.09 (1H, m), 2.74—2.77 (4H, m), 2.93 (2H, d, J=7.4 Hz), 4.03 (1H, t, J=7.4 Hz), 5.20 (1H, s), 5.39 (1H, s), 7.26—7.43 (5H, m). HRMS Found: m/z 236.0693. Calcd for $C_{13}H_{16}S_2$: M, 236.0695.

2-(4-Pentenyl)-2-phenacyl-1,3-dithiane (6). Colorless oil; IR (neat) 2906, 1687, 1641, 760, 694 cm^{-1}; ^{1}H NMR δ=1.52—1.58 (2H, m), 1.88—1.92 (2H, m), 1.99—2.03 (2H, m), 2.14—2.17 (2H, m), 2.76—2.79 (4H, m), 3.51 (2H, s), 4.87—4.90 (1H, m), 4.92—4.97 (1H, m), 5.68—5.75 (1H, m), 7.38—7.41 (2H, m), 7.48—7.51 (1H, m), 7.88—7.90 (2H, m). HRMS Found: m/z 306.1109. Calcd for $C_{17}H_{22}OS_2$: M, 306.1114.

2-Methyl-2-phenacyl-1,3-dithiane (9a). Colorless oil; IR (neat) 2902, 1674, 756, 692 cm^{-1}; ^{1}H NMR δ=1.83 (3H, s), 1.91—2.04 (2H, m), 2.81—2.91 (4H, m), 3.58 (2H, s), 7.42—7.46 (2H, m), 7.53—7.55 (1H, m), 7.93—7.95 (2H, m). Found: C, 61.84; H, 6.32; S, 25.03%. Calcd for $C_{13}H_{16}OS_2$: C, 61.86; H, 6.39; S, 25.41%.

2-Methyl-2-(2-oxocyclopentyl)-1,3-dithiane (9i). Colorless oil; IR (neat) 2966, 1738 cm^{-1}; ^{1}H NMR δ= 1.63—1.71 (1H, m), 1.81—1.89 (1H, m), 1.84 (3H, s), 1.96—2.07 (2H, m), 2.08—2.19 (2H, m), 2.29—2.35 (2H, m), 2.54—2.58 (1H, m), 2.68—2.75 (2H, m), 2.94—3.02 (2H, m); ^{13}C NMR δ=19.78, 24.88, 25.54, 26.20, 26.37, 27.01, 40.35, 50.89, 56.44, 215.86. HRMS Found: m/z 216.0649. Calcd for $C_{10}H_{16}OS_2$: M, 216.0644.

2-Methyl-2-(3-methyl-2-oxobutyl)-1,3-dithiane (9b). Colorless oil; IR (neat) 2964, 1707 cm^{-1}; ^{1}H NMR d=1.11 (6H, d, J=6.9 Hz), 1.82 (3H, s), 1.92—2.04 (2H, m), 2.74 (1H, sept, J=6.9 Hz), 2.88—2.91 (4H, m), 3.10 (2H, s). HRMS Found: m/z 218.0807. Calcd for $C_{10}H_{18}OS_2$: M, 218.0800.

Ethyl 2-Methyl-1,3-dithiane-2-acetate (9e). Colorless oil; IR (neat) 2927, 1734, 1194 cm^{-1}; ^{1}H NMR δ=1.28 (3H, t, J=7.1 Hz), 1.77 (3H, s), 1.85—1.91 (1H, m), 2.07—2.12 (1H, m), 2.72—2.78 (2H, m), 3.01—3.09 (2H, m), 3.02 (2H, s), 4.17 (2H, q, J=7.1 Hz). HRMS Found: m/z 220.0610. Calcd for $C_9H_{16}O_2S_2$: M, 220.0593.

2-Phenacyl-2-phenyl-1,3-dithiane (11a). Colorless crystals; mp 119.0—119.5 °C (hexane–ethyl acetate); IR (KBr) 1676, 764, 690 cm^{-1}; ^{1}H NMR δ=1.91—1.99 (2H, m) 2.68—2.79 (4H, m), 3.66 (2H, s), 7.17—7.20 (1H, m), 7.27—7.32 (4H, m), 7.44—7.47 (1H, m), 7.72—7.73 (2H, m), 7.94—7.96 (2H, m). Found: C, 68.49; H, 5.64; S, 19.99%. Calcd for $C_{18}H_{18}OS_2$: C, 68.75; H, 5.77; S, 20.39%.

2-(2-Oxocyclopentyl)-2-phenyl-1,3-dithiane (11i). Colorless crystals; mp 109.5—110.0 °C (hexane–ethyl acetate); IR (KBr) 2902, 1736, 706 cm^{-1}; ^{1}H NMR δ= 1.51—1.58 (1H, m), 1.63—1.70 (1H, m), 1.73—1.82 (1H, m), 1.89—2.00 (3H, m), 2.09—2.17 (2H, m), 2.60—2.65 (3H, m), 2.72—2.78 (2H, m), 7.26—7.29 (1H, m), 7.37—7.40 (2H, m), 7.97—7.99 (2H, m). Found: C, 64.43; H, 6.40; S, 23.45%. Calcd for $C_{15}H_{18}OS_2$: C, 64.71; H, 6.52; S, 23.03%.

2-(3-Methyl-2-oxobutyl)-2-phenyl-1,3-dithiane (11b). Colorless crystals; mp 64.0—65.0 °C (hexane); IR (KBr) 2908, 1709, 760, 702 cm^{-1}; ^{1}H NMR δ=0.86 (6H, d, J=6.9 Hz), 1.92—1.99 (2H, m), 2.23 (1H, sept, J=6.9 Hz), 2.67—2.78 (4H, m), 3.16 (2H, s), 7.26—7.28 (1H, m), 7.36—7.39 (2H, m), 7.94—7.95 (2H, m). Found: C, 64.00; H, 6.98%. Cald for $C_{15}H_{20}OS_2$: C, 64.24; H, 7.19%. HRMS Found: m/z 280.0956. Calcd for $C_{15}H_{20}OS_2$: M, 280.0957.

Ethyl 2-Phenyl-1,3-dithiane-2-acetate (11e). Colorless oil; IR (neat) 2904, 1734, 1190, 756, 700 cm^{-1}; ^{1}H NMR δ=1.05 (3H, t, J=7.2 Hz), 1.92—2.05 (2H, m), 2.72—2.80 (4H, m), 3.09 (2H, s), 3.95 (2H, q, J=7.2 Hz), 7.26—7.29 (1H, m), 7.36—7.40 (2H, m), 7.92—7.94 (2H, m). Found: C, 59.28; H, 6.39; S, 22.59%. Calcd for $C_{14}H_{18}O_2S_2$: C, 59.54; H, 6.42; S, 22.71%.

3,3-Bis(methylthio)-1-phenyl-1-propanone (13a). Colorless oil; IR (neat) 2918, 1695, 762, 690 cm^{-1}; ^{1}H NMR δ=2.17 (6H, s), 3.44 (2H, d, J=6.9 Hz), 4.39 (1H, t, J=6.9 Hz), 7.45—7.49 (2H, m), 7.56—7.59 (1H, m), 7.94—7.96 (2H, m). Found: C, 58.45; H, 6.24; S, 28.65%. Calcd for $C_{11}H_{14}OS_2$: C, 58.37; H, 6.23; S, 28.33%.

4-Methyl-1,1-bis(methylthio)-3-pentanone (13b). Colorless oil; IR (neat) 2974, 1714 cm^{-1}; ^{1}H NMR δ=1.12 (6H, d, J=6.9 Hz), 2.14 (6H, s), 2.60 (1H, sept, J=6.9 Hz), 2.91 (2H, d, J=7.0 Hz), 4.22 (1H, t, J=7.0 Hz). Found: C, 49.71; H, 8.10; S, 33.63%. Calcd for $C_8H_{16}OS_2$: C, 49.96; H, 8.38; S, 33.34%.

2-Phenacyl-1,3-benzodithiole (15a). Pale yellow crystals; mp 123.0—123.5 °C (hexane); IR (KBr) 1674, 756 cm^{-1}; ^{1}H NMR δ=3.68 (2H, d, J=7.0 Hz), 5.36 (1H, t, J= 7.0 Hz), 7.03—7.05 (2H, m), 7.21—7.24 (2H, m), 7.43—7.47 (2H, m), 7.56—7.59 (1H, m), 7.91—7.93 (2H, m). HRMS Found: C, 65.84; H, 4.36; S, 23.64%. Calcd for $C_{15}H_{12}OS_2$: C, 66.14; H, 4.44; S, 23.54%.

Ethyl 1,3-Benzodithiole-2-acetate (15e). Colorless oil; IR (neat) 2979, 1734, 1444, 1205, 744 cm^{-1}; ^{1}H NMR δ=1.27 (3H, t, J=7.1 Hz), 2.96 (2H, d, J=7.5 Hz), 4.18 (2H, q, J=7.1 Hz), 5.10 (1H, t, J=7.5 Hz), 7.03—7.06 (2H, m), 7.21—7.24 (2H, m). HRMS Found: m/z 240.0271. Calcd for $C_{11}H_{12}O_2S_2$: M, 240.0280.

Preparation of Tributyl(phenylthiomethyl)stannane (16). Tributyl(phenylthiomethyl)stannane (**16**) was prepared according to the literature procedure.[28]

Preparation of Phenyl α-Tributylstannylbenzyl Sulfide (17). To a THF solution (40 ml) of benzyl phenyl sulfide (3.50 g, 17.5 mmol) was added dropwise butyllithium (14 ml, 1.6 mol dm^{-3} in hexane, 22 mmol) at −78 °C.[29] The solution became yellow. After being stirred for 30 min at 0 °C, the solution was cooled to −78 °C, and then tributylchlorostannane (6.2 ml, 23 mmol) was added. The reaction mixture was stirred overnight and allowed to warm to room temperature. The reaction was quenched with water, and insoluble materials were removed by filtration through a celite pad, which was washed several times with hexane. The organic phase was separated and the aqueous phase was extracted with hexane three times. The combined extracts were dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure. The residue was purified by silica-gel column chromatography to afford the product **17** (6.67 g, 13.6 mmol, 78%).

Methyl α-tributylstannylbenzyl sulfide (**19**) was prepared from benzyl methyl sulfide in the same manner (74% yield).

Phenyl α-Tributylstannylbenzyl Sulfide (17). Colorless oil; IR (neat) 3059, 2956, 1589, 1483, 739, 694 cm^{-1}; ^{1}H NMR δ=0.86 (9H, t J=7.3 Hz), 0.90—1.00 (6H, m), 1.23—1.30 (6H, m), 1.38—1.50 (6H, m), 4.12 (1H, s), 6.98—7.01 (2H, m), 7.10—7.20 (6H, m), 7.29—7.31 (2H, m). Found: C, 61.21; H, 7.62; S, 6.52%. Calcd for $C_{25}H_{38}SSn$: C, 61.36; H, 7.83; S, 6.55%.

Methyl α-Tributylstannylbenzyl Sulfide (19). Colorless oil; IR (neat) 2956, 1595, 1456, 773, 696 cm^{-1}; ^{1}H NMR δ=0.71—0.96 (15H, m), 1.20—1.27 (6H, m), 1.32—1.46 (6H, m), 1.89 (3H, s), 3.51 (1H, s), 7.01—7.04 (1H, m), 7.20—7.24 (4H, m). Found: C, 56.28; H, 8.27; S, 8.00%. Calcd for $C_{20}H_{36}SSn$: C, 56.22; H, 8.49; S, 7.50%.

Preparation of Phenyl 1-Tributylstannyl-3-phenylpropyl Sulfide (21). To a THF solution (50 ml) of diisopropylamine (3.2 g, 32 mmol) was added dropwise butyllithium (20 ml, 1.6 mol dm^{-3} in hexane, 32 mmol) at 0 °C. After being stirred for 30 min at 0 °C, tributyltin hydride (8.1 ml, 30 mmol) was added,[30] and the solution was stirred for 15 min. The solution was cooled to −78 °C, and then a THF solution (10 ml) of 3-phenylpropanal (4.0 g, 30 mmol) was added. The reaction mixture was stirred for 30 min, and turned deep yellow in the meantime. To this yellow solution, methanesulfonyl chloride (2.6 ml, 34 mmol) was added and immediately thiophenol (4.0 ml, 39 mmol) was added.[31] The reaction mixture was stirred overnight and allowed to warm to room temperature. The reaction was quenched with water, and extracted with hexane three times. The combined extracts were washed successively with aq NaOH, water, and brine. After dried over anhydrous sodium sulfate, the solvent was removed under reduced pressure. The residue was purified by silica-gel column chromatography to afford the product **21** (8.7 g, 16.8 mmol, 56%).

Spectral data and physical properties are as follows: Colorless oil; IR (neat) 3062, 2924, 1458, 741, 694 cm^{-1}; ^{1}H NMR δ=0.94 (9H, t, J=7.3 Hz), 1.00—1.13 (6H, m), 1.34—1.42 (6H, m), 1.53—1.63 (6H, m), 2.10—2.15 (2H, m), 2.49—2.55 (1H, m), 2.85—2.91 (1H, m), 3.09 (1H, t, J=5.8 Hz), 7.10—7.32 (10H, m). Found: C, 62.90; H, 8.18; S, 6.75%. Calcd for $C_{27}H_{42}SSn$: C, 62.68; H, 8.18; S, 6.20%.

Typical Procedure for the Reaction of 1-(Tributylstannyl)alkyl Sulfide with Olefinic Nucleophiles. The reaction between phenyl α-tributylstannylbenzyl sulfide (**17**) and the silyl enol ether **2a** was carried out in the same procedure for 2-tributylstannyl-1,3-dithiane (**4**), using 99.5 mg of **17** (0.203 mmol), 83.2 mg of **2a** (0.434 mmol), and 233.3 mg of CAN (0.426 mmol). The product **18a** was obtained in 83% yield (53.5 mg, 0.168 mmol).

Spectral data and physical properties of the products are as follows.

1,3-Diphenyl-3-phenylthio-1-propanone (18a). Colorless crystals; mp 114.0—115.0 °C (hexane–ethyl acetate); IR (KBr) 1678, 744, 692 cm^{-1}; ^{1}H NMR δ=3.58 (1H, dd, J=5.9, 17.2 Hz), 3.65 (1H, dd, J=8.2, 17.2 Hz), 4.95 (1H, dd, J=5.9, 8.2 Hz), 7.16—7.56 (13H, m), 7.87—7.89 (2H, m). Found: C, 78.97; H, 5.83; S, 9.86%. Calcd for $C_{21}H_{18}OS$: C, 79.21; H, 5.70; S, 10.07%.

4-Methyl-1-phenyl-1-phenylthio-3-pentanone (18b). Colorless crystals; mp 56.0—56.5 °C (methanol); IR (KBr) 2968, 1701, 741, 696 cm^{-1}; ^{1}H NMR δ=0.93 (3H, d, J=6.9 Hz), 1.01 (3H, d, J=6.9 Hz), 2.46 (1H, qq, J=6.9, 6.9 Hz), 3.04 (1H, dd, J=6.3, 17.0 Hz), 3.08 (1H, dd, J=8.1, 17.0 Hz), 4.77 (1H, dd, J=6.3, 8.1 Hz), 7.16—7.29 (10H, m). Found: C, 76.10; H, 7.02; S, 11.11%. Calcd for $C_{18}H_{20}OS$: C, 76.01; H, 7.09; S, 11.27%.

2-Methyl-1,3-diphenyl-3-phenylthio-1-propanone (18c). Diastereomer mixture (40 : 60); colorless oil; IR (neat) 3059, 2974, 1680, 970, 746, 696 cm^{-1}; ^{1}H NMR δ= 0.99 (3H×0.4, d, J=6.9 Hz), 1.53 (3H×0.6, d, J=6.9 Hz), 4.02 (1H×0.4, dq, J_d=10.3, J_q=6.9 Hz), 4.08 (1H×0.6, dq, J_d=10.1, J_q=6.6 Hz), 4.53 (1H×0.4, d, J=10.3 Hz), 4.58 (1H×0.6, d, J=10.1 Hz), 7.00—7.27 (9H×0.4+11H×0.6, m), 7.34—7.37 (1.2H, m), 7.46—7.52 (1.2H, m), 7.58—7.61 (1H×0.4, m), 7.74—7.76 (2H×0.6, m), 8.02—8.05 (2H×0.4, m). HRMS Found: m/z 332.1233. Calcd for $C_{22}H_{20}OS$: M, 332.1236.

Ethyl 3-Phenyl-3-phenylthiopropanoate (18e). Colorless oil; IR (neat) 2983, 1736, 1151, 748, 698 cm^{-1}; ^{1}H NMR δ=1.13 (3H, t, J=7.2 Hz), 2.91 (1H, dd, J=8.3, 15.7 Hz), 2.93 (1H, dd, J=7.2, 15.7 Hz), 4.027 (1H, dq, J_d=9.5, J_q=7.2 Hz), 4.033 (1H, dq, J_d=9.5, J_d=7.2 Hz), 4.64 (1H, dd, J=7.2, 8.3 Hz), 7.18—7.31 (10H, m). Found: C, 71.18; H, 6.37; S, 11.45%. Calcd for $C_{17}H_{18}O_2S$: C, 71.30; H, 6.33; S, 11.20%.

4-Phenyl-4-phenylthio-1-butene (18f). Colorless oil; IR (neat) 3062, 2916, 1639, 1481, 1442, 742, 696 cm^{-1}; ^{1}H NMR δ=2.67—2.76 (2H, m), 4.19 (1H, t-like dd), 4.98—5.05 (2H, m), 5.68—5.76 (1H, m), 7.17—7.27 (10H, m). HRMS Found: m/z 240.0961. Calcd for $C_{16}H_{16}S$: M, 240.0974.

3-Methylthio-1,3-diphenyl-1-propanone (20a). Colorless crystals; mp 56.5—57.0 °C (hexane–ethyl acetate); IR (KBr) 1684, 1446, 756, 694 cm^{-1}; ^{1}H NMR δ=1.93 (3H, s), 3.55 (2H, d, J=7.0 Hz), 4.46 (1H, t, J=7.0 Hz), 7.20—7.24 (1H, m), 7.29—7.32 (2H, m), 7.39—7.46 (4H, m), 7.51—7.56 (1H, m), 7.91—7.93 (2H, m). Found: C, 74.76; H, 6.19; S, 12.15%. Calcd for $C_{16}H_{16}OS$: C, 74.96, H, 6.29; S, 12.51%.

4-Methyl-1-methylthio-1-phenyl-3-pentanone (20b). Colorless oil; IR (neat) 2970, 1712, 766, 702 cm^{-1}; ^{1}H NMR δ=0.96 (3H, d, J=6.9 Hz), 1.05 (3H, d, J=6.9 Hz), 1.89 (3H, s), 2.50 (1H, qq, J=6.9, 6.9 Hz), 3.00 (2H, d, J=7.2 Hz), 4.27 (1H, t, J=7.2 Hz), 7.20—7.34 (5H, m). Found: C, 70.39; H, 7.89; S, 14.04%. Calcd for $C_{13}H_{18}OS$: C, 70.22; H, 8.16; S, 14.42%.

1,5-Diphenyl-3-phenylthio-1-pentanone (22a). Colorless oil; IR (neat) 3059, 2922, 1684, 1448, 750, 690 cm^{-1}; ^{1}H NMR δ=1.90 (1H, dddd, J=5.3, 8.4, 10.1, 12.1 Hz), 2.03 (1H, dddd, J=4.9, 6.3, 10.1, 12.1 Hz), 2.80 (1H, ddd, J=6.3, 10.1, 16.3 Hz), 2.92 (1H, ddd, J=5.3, 10.1, 16.3 Hz), 3.18 (1H, dd, J=8.0, 17.0 Hz), 3.30 (1H, dd, J=5.5, 17.0 Hz), 3.81 (1H, dddd, J=4.9, 5.5, 8.0, 8.4 Hz), 7.14—7.17 (3H, m), 7.21—7.29 (5H, m), 7.41—7.45 (4H, m), 7.52—7.55 (1H, m), 7.83—7.85 (2H, m). Found: C, 79.70; H, 6.48; S, 9.38%. Calcd for $C_{23}H_{22}OS$: C, 79.73; H, 6.40; S, 9.25%.

2-Methyl-7-phenyl-5-phenylthio-3-heptanone (22b). Colorless oil; IR (neat) 2968, 1711, 1465, 746, 700 cm^{-1}; ^{1}H NMR δ=1.02 (3H, d, J=6.9 Hz), 1.04 (3H, d, J=6.9 Hz), 1.81 (1H, dddd, J=5.4, 8.2, 10.2, 17.0 Hz), 1.90 (1H, dddd, J=5.0, 6.3, 10.2, 17.0 Hz), 2.50 (1H, qq, J=6.9 Hz), 2.68 (1H, dd, J=7.5, 17.4 Hz), 2.73 (1H, ddd, J=6.3, 10.2, 13.8 Hz), 2.78 (1H, dd, J=5.9, 17.4 Hz), 2.84 (1H, ddd, J=5.4, 10.2, 13.8 Hz), 3.63 (1H, dddd, J=5.0, 5.9, 7.5, 8.2 Hz), 7.13—7.20 (3H, m), 7.21—7.28 (5H, m), 7.37—7.39 (2H, m). Found: C, 76.60; H, 7.73; S, 9.89%. Calcd for $C_{20}H_{24}OS$: C, 76.88; H, 7.74; S, 10.26%.

Ethyl 5-Phenyl-3-phenylthiopentanoate (22e).

Colorless oil; IR (neat) 2929, 1734, 1240, 1153, 746, 698 cm^{-1}; ^{1}H NMR δ=1.22 (3H, t, J=7.2 Hz), 1.84 (1H, dddd, J=5.4, 8.5, 9.8, 17.4 Hz), 1.94 (1H, dddd, J=5.0, 6.5, 9.8, 17.4 Hz), 2.54 (1H, dd, J=7.5, 15.6 Hz), 2.61 (1H, dd, J=6.8, 15.6 Hz), 2.78 (1H, ddd, J=6.5, 9.8, 13.8 Hz), 2.89 (1H, ddd, J=5.4, 9.8, 13.8 Hz), 3.48 (1H, dddd, J=5.0, 6.8, 7.5, 8.5 Hz), 4.06—4.12 (2H, m), 7.15—7.19 (3H, m), 7.23—7.30 (5H, m), 7.41—7.44 (2H, m). HRMS Found: m/z 314.1342. Calcd for $C_{19}H_{22}O_2S$: M, 314.1342.

6-Phenyl-4-phenylthio-1-hexene (22g). Colorless oil; IR (neat) 2929, 1581, 1438, 744, 696 cm^{-1}; ^{1}H NMR δ=1.78—1.86 (1H, m), 1.90—1.97 (1H, m), 2.31—2.42 (2H, m), 2.78 (1H, ddd, J=6.5, 9.5, 13.8 Hz), 2.83 (1H, ddd, J=5.9, 9.6, 13.8 Hz), 3.11—3.16 (1H, m), 5.04—5.08 (2H, m), 5.80—5.89 (1H, m), 7.15—7.28 (8H, m), 7.35—7.38 (2H, m). HRMS Found: m/z 268.1278. Calcd for $C_{18}H_{20}S$: M, 268.1287.

Benzyl Phenyl Sulfoxide (25). Colorless crystals; mp 121—122 °C (hexane–ethyl acetate), lit,[32] 123—124 °C; IR (KBr) 1038, 746, 694 cm^{-1}; ^{1}H NMR δ=3.97 (1H, d, J=12.6 Hz), 4.07 (1H, d, J=12.6 Hz), 6.95—6.97 (2H, m), 7.21—7.26 (3H, m), 7.34—7.44 (5H, m).

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