Differentiation between Carbonyls and Acetals in 1,3-Dithiane and 1,3-Dithiolane Synthesis Catalyzed by Organotin Triflates

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Received February 26, 1993

Carbonyls and acetals are converted to 1,3-dithianes and -dithiolanes upon treatment with 2-stanna-1,3-dithianes and -dithiolanes under catalysis by organotin triflates. In these competition reactions, various types of carbonyls and acetals are differentiated. Aldehydes react preferentially over ketones, but the preference is completely reversed in the competition reactions between the corresponding acetals and ketals. The reactivity of aliphatic aldehydes is greater than that of the acetals of aliphatic aldehydes and ketones. Conversely, an aromatic acetal is more reactive than its parent aldehyde. In the competition between aromatic and aliphatic aldehydes, the reaction of the latter predominates. However, aromatic acetals react preferentially over aliphatic acetals. Ketones of different types are also differentiated. No such discrimination can be achieved by conventional methods. Organotin triflates are capable of detecting subtle differences in the reactivity of carbonyls and acetals. Such unique differentiation can be explained in terms of the dependence of the reaction path on the substrate: the reactions of carbonyls are initiated by coordination to tin, whereas the reactions of acetals proceed via oxocarbenium ion intermediates.

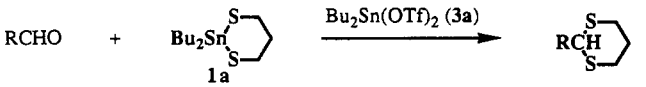
The chemical transformation of a carbonyl group is one of the fundamental manipulations in organic synthesis. However, molecules bearing multiple carbonyl groups are frequently encountered. In those cases, the carbonyl group being modified must be differentiated from the other carbonyls and from acetals and ketals, which can also be considered as members of the carbonyl family. Differentiation such as aldehyde (or its acetal) vs ketone (or its ketal), aldehyde (or its acetal) vs aldehyde (or its acetal), ketone (or its ketal) vs ketone (or its ketal), and aldehyde or ketone vs acetal have recently been the subject of considerable attention.[1]

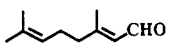
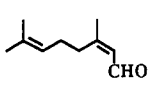
1,3-Dithianes are masked carbonyls that are especially useful because of their ability to undergo further carbon–carbon bond formation.[2] 1,3-Dithiolanes are also often used for protecting ketones.[3] Hence, selective dithioacetalizations of carbonyl functions are of great synthetic value. Previously, we disclosed that carbonyls and acetals undergo smooth thioacetalization when exposed to thiostannanes in the presence of a Lewis acid.[4] Also noteworthy is the usefulness of organotin triflates. These catalysts, due to their mild Lewis acidity, allow selective transformations of carbonyls and acetals.[5] Evans et al. have used 1,2-bis[(trimethylsilyl)thio]ethane in the presence of ZnI_2 for the selective dithioacetalization of one ketonic function, particularly for steroid derivatives.[6] Carbonyl differentiation in dithioacetalization has also been reported in some cases.[7] Herein, we demonstrate the efficiency of the organotin triflate–thiostannane methodology for various types of the aforementioned differentiating operations as well as its synthetic potential for the preparation of 1,3-dithianes and 1,3-dithiolanes.[8]

Results and Discussion

First, we determined the synthetic utility of our method. Treatment of aldehydes with thiostannane **1a** (1.2 equiv) in the presence of $Bu_2Sn(OTf)_2$ (**3a**) in 1,2-dichloroethane afforded the desired 1,3-dithianes in reasonable yields (Table I). These compounds are conventionally prepared with 1,3-propanedithiol under acidic conditions and are occasionally contaminated by yellow byproducts. Fortunately, no such byproducts were detected in our reactions. Of more synthetic value than the absence of byproducts is the mildness of the reaction; acid-labile substrates could be successfully employed (Table I, entries 3, 5–7). When aldehydes having a siloxy or tetrahydropyranyloxy group were subjected to the conventional reaction, these protecting groups were unmasked considerably or completely (eqs 1 and 2). Unfortunately, however, the α,β-enals screened in this study underwent isomerization (Table I, entries 9–11). The reactions with

Table I. Synthesis of 1,3-Dithianes from Aldehydes[a]



entry	RCHO	reaction temp, °C	reaction time, h	yield,[b] %	E:Z
1	BuCHO	35	20	(99)	
2	PhCHO	35	20	73 (100)	
3	furfural	35	20	85 (100)	
4	$AcO(CH_2)_5CHO$	0	0.5[c]	79	
5	$THPO(CH_2)_5CHO$	−40	3[c,d]	63[e] [77][f]	
6	$^tBuMe_2SiO(CH_2)_5CHO$	−30	3[c,d]	80[e] [92][f]	
7	$^tBuPh_2SiO(CH_2)_5CHO$	0	0.5[c]	94	
8		35	12	69	
9		35	12	97	89:11[g]
10		35	12	56 [83]	60:40[h]
11		35	12	59 [86]	60:40[h]

[a] Reaction conditions: aldehyde (0.5 mmol); **1a** (0.6 mmol); **3a** (0.15 mmol); $ClCH_2CH_2Cl$ (4 mL) unless otherwise noted. [b] Isolated yields. GLC yields are given in parentheses. [c] **3a** (0.6 mmol) was employed. [d] Toluene (3 mL) was used as a solvent. [e] The siloxy group was hydrolyzed to a small extent (7%). [f] A small amount of the starting material remained unchanged. The yield based on the consumed starting material is indicated in the brackets. [g] Determined by NMR. [h] Determined by GLC.

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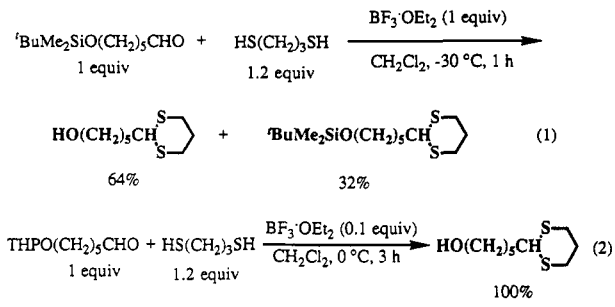
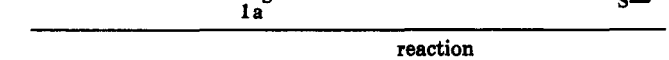


acetals proceeded smoothly, and the results of these reactions are compiled in Table II. 1,3-Dithiolanes were readily obtained by treating ketones and a ketal with thiostannane **2a** (Table III). It follows from these results that the organotin triflate–thiostannane methodology is truly effective for the dithioacetalization of carbonyls and acetals. In some respects, our method is comparable to the Evans' thiosilane protocol, which, however, was applied to carbonyls only: no reaction with acetals was described. Moreover, the following merits of our method are worthy of note. Thiostannanes can be readily prepared from various organotin sources such as oxides, alkoxides, and halides.[9] They are entirely air- and moisture-stable and, thus, can be used even in the presence of water. Of more

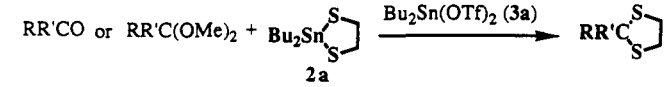
Table II. Synthesis of 1,3-Dithianes from Acetals[a]

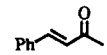
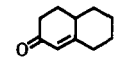
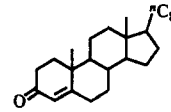


entry	$RR'C(OR)_2$	reaction temp, °C	reaction time, h	yield,[b] %	E/Z
1	$BuCH(OMe)_2$	35	3	(92)	
2	$^nC_8H_{17}CH(OMe)_2$	35	20	87	
3	cyclo-$C_6H_{11}CH(OMe)_2$	35	20	88 (91)	
4	$PhCH(OMe)_2$	35	20	74 (100)	
5		35	20	(79)	
6	(*E*)-$PrCH{=}CHCH(OMe)_2$	35	1	81	100:0[c]
7	(*E*)-$PhCH{=}CHCH(OMe)_2$	35	1	84 (93)	100:0[c]
8	$(^nC_4H_9)MeC(OMe)_2$	35	3	75 (87)	

[a] Reaction conditions: acetal (1 mmol); **1a** (1.2 mmol); **3a** (0.3 mmol); $ClCH_2CH_2Cl$ (8 mL) unless otherwise noted. [b] Isolated yields. GLC yields are given in parentheses. [c] Determined by GLC.

Table III. Synthesis of 1,3-Dithiolanes[a]



entry	RCHO	3a (equiv)	reaction temp, °C	reaction time, h	yield, %[b]
1	$(^nC_5H_{11})MeCO$	0.7	35	20	(74)
2	PhMeCO	1.4	35	20	(10)
3	$PhMeC(OMe)_2$	1.4	35	1	(79)
4		0.5	35	20	74
5		0.7	35	10	83 (100)
6		1.7[c]	20	14	84[d]
7		1.7[c]	20	20	99[d]
8		1.7[c]	20	24	81[d]

[a] Reaction conditions: ketone or acetal (0.3 mmol); **2a** (0.36 mmol); $ClCH_2CH_2Cl$ (2 mL) unless otherwise noted. [b] Isolated yields. GLC yields are given in parentheses. [c] **2a** (0.51 mmol) was employed. [d] No isomerization of the double bond occurred.

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Org. Chem.* **1978**, *43*, 3977. Luche, J.; Gemal, A. L. *J. Am. Chem. Soc.* **1979**, *101*, 5848. Gemal, A. L.; Luche, J. *J. Org. Chem.* **1979**, *44*, 4187. Kraus, G. A.; Frazier, K. *J. Org. Chem.* **1980**, *45*, 4262. Yamaguchi, S.; Kabuto, K.; Yasuhara, F. *Chem. Lett.* **1981**, 461. Krishnamurthy, S. *J. Org. Chem.* **1981**, *46*, 4628. Gemal, A. L.; Luche, J. *J. Am. Chem. Soc.* **1981**, *103*, 5454. Gemal, A. L.; Luche, J. *Tetrahedron Lett.* **1981**, *22*, 4077. Keinan, E.; Gleize, P. A. *Tetrahedron Lett.* **1982**, *23*, 477. Babler, J. H.; Sarussi, S. J. *J. Org. Chem.* **1983**, *48*, 4416. Nutaitis, C. F.; Gribble, G. W. *Tetrahedron Lett.* **1983**, *24*, 4287. Yoon, N. M.; Park, K. B.; Gyoung, Y. S. *Tetrahedron Lett.* **1983**, *24*, 5357. Kim, S.; Kang, H. J.; Yang, S. *Tetrahedron Lett.* **1984**, *25*, 2985. Huang, Y.; Shen, Y.; Chen, C. *Tetrahedron Lett.* **1985**, *26*, 5171. Varma, R. S.; Kabalka, G. W. *Synth. Commun.* **1985**, *15*, 985. Yoon, N. 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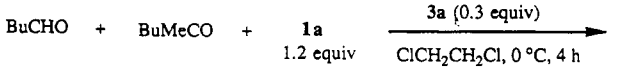
practical significance is the fact that, because of their odorlessness, they can be stored in open air.

Differentiation. With the basic data discussed above in hand, we next turned our attention to the otherwise difficult-to-achieve differentiation between various types of carbonyls and acetals.

I. Competition between Aldehydes (or Acetals) and Ketones (or Ketals). When an equimolar mixture of pentanal and 2-hexanone was exposed to **1a** (1.2 equiv) and **3a** (0.3 equiv) in 1,2-dichloroethane at 0 °C, the former substrate was converted to the desired 1,3-dithiane in 74% yield and the latter was completely unchanged (eq 3). The



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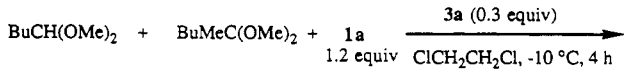
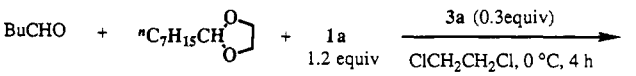


(4)

preference was totally reversed in the reaction of the corresponding acetal and ketal (eq 4). This type of bias, also observed in the organotin triflate-catalyzed aldol reaction of enol silyl ethers,[5a] seems to reflect a different reaction mechanism for each type of substrate. Namely, the reaction of the carbonyl is initiated by coordination of the carbonyl to tin. Thus, the enhanced reactivity of the aldehyde can be accounted for by the fact that the aldehyde forms a complex with tin more readily than the ketone does.[10] In contrast, the reaction of the acetal proceeds via an oxocarbenium ion, which is generated from ketals more easily than from aldehyde competitors.[11]

Remarkably, the organotin triflate catalyst is able to detect subtle differences between the substrates in both reaction paths. All of the differentiations that follow can be understood in terms of these two mechanisms.

II. Competition between Carbonyls and Acetals. Competition between pentanal and an ethylene acetal of octanal or 2-hexanone resulted in preferential dithioacetalization of the aldehyde component (eqs 5 and 6), and



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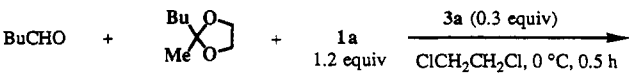

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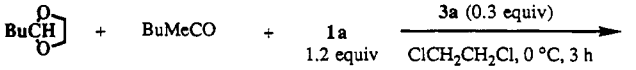
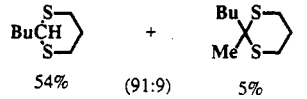
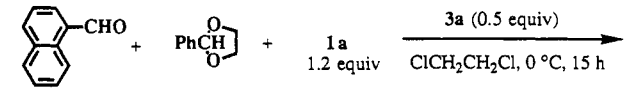
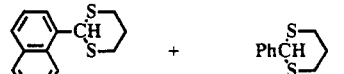




(7)

an ethylene acetal of pentanal reacted preferentially over 2-hexanone (eq 7). Apparently, the reactivity of an aliphatic aldehyde is greater than that of the corresponding acetal, whereas the reactivity of an aliphatic ketone is much lower than that of an acetal. Conversely, an aromatic acetal reacted much faster than an unmasked aldehyde (eq 8), the expected outcome on the basis of the facile formation of the oxocarbenium ion from the aromatic acetals.





(8)

III. Competition between Aldehydes. Differentiation between two of the same type of carbonyl functions requires highly elaborated methods. Organotin triflates effect such differentiations successfully. As shown in Scheme I, competition between benzaldehyde and pentanal led to predominant formation of the 1,3-dithiane of the latter. As a control experiment, the reaction was conducted under three different conditions: $HS(CH_2)_3SH/BF_3{\cdot}OEt_2$, **1a**/$BF_3{\cdot}OEt_2$, $HS(CH_2)_3SH$/**3a**. All three reactions resulted in the same preference but much lower selectivities. Obviously, the combined use of **1a** and **3a** is indispensable for the high selectivity. Pentanal reacted preferentially over 1-naphthaldehyde. Benzaldehyde reacted more sluggishly than *p*-anisaldehyde but faster than *p*-nitrobenzaldehyde. These results are all consistent with the initial coordination of the carbonyl to tin.[12]

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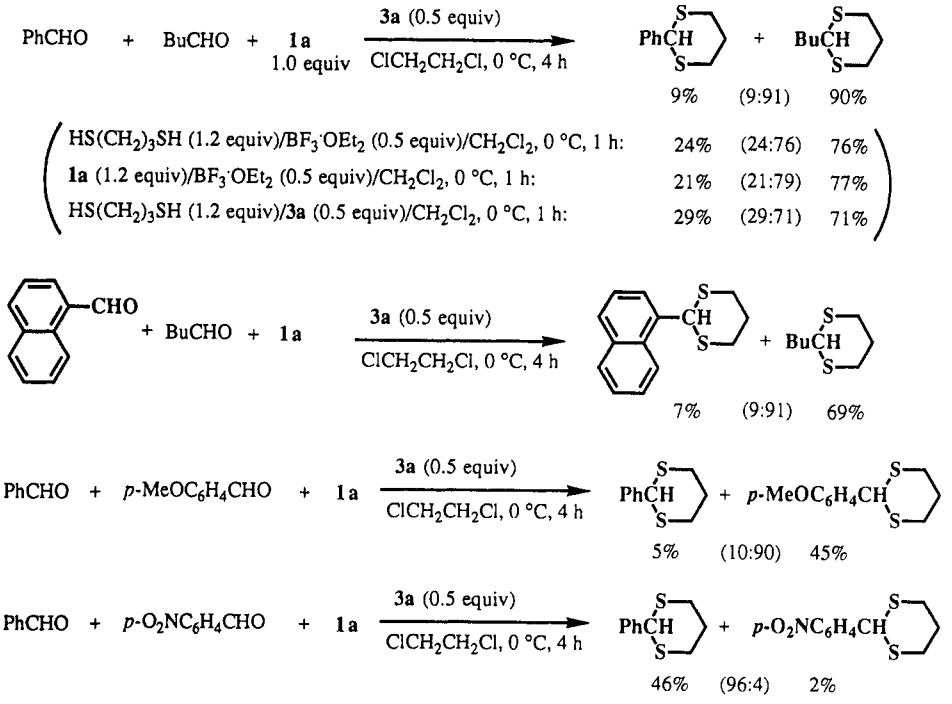
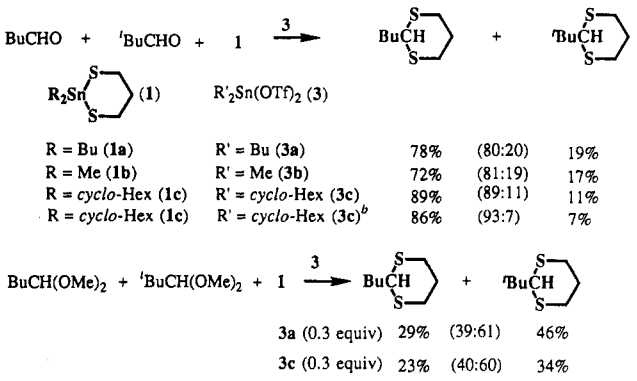
Scheme I[a]



[a] **1a** (1.2 equiv) was used.

Scheme II[a]



[a] **1** (1.2 equiv) and **3** (0.5 equiv) were used. [b] In CH_3CN.

In addition to the electronic effects discussed above, steric effects also delivered confirmatory evidence for the initial coordination of the carbonyl to tin (Scheme II). For the competition between pentanal and pivalaldehyde, the less bulky 1,3-dithiane was favored when **1a** and **3a** were used. The methyl derivatives of the triflate (**1b**) and the thiostannane (**3b**) gave rise to little change in the selectivity. However, the selectivity was increased by a considerable degree when bulky cyclohexyl derivatives **1c** and **3c** were used. This increase in selectivity indicates the importance of steric hindrance between the substrate and the catalyst. As expected, no such increase in selectivity was observed in the reaction with acetals, even when **1c**/**3c** were used.

IV. Competition between Acetals. Aromatic acetals could also be differentiated from aliphatic ones (Scheme III). Acetals of benzaldehyde and furfural reacted preferentially over pentanal dimethyl acetal. The intermediacy of the oxocarbenium ion in this class of reaction was supported by the results of the competition reactions between acetals of benzaldehyde and its para-substituted derivatives. An electron-withdrawing group suppressed the reaction, and an electron-donating group accelerated the reaction. A dimethyl acetal of an α-enal reacted preferentially over pentanal dimethyl acetal. Of course, the reaction of the enal and pentanal, their parent aldehydes, which proceeds by the coordination mechanism, failed to give rise to the high selectivity.

V. Competition between Ketones. Differentiation between ketones was tested with the 1,3-dithiolane synthesis (Scheme IV). Cyclohexanone was found to react preferentially over 2-heptanone, cyclopentanone, and 2-methylcyclohexanone. Notably, no such high selectivities were attained by the conventional method employing $HS(CH_2)_2SH$ and $BF_3{\cdot}OEt_2$ in any cases. The validity of the coordination mechanism was again proved by the increased selectivity for the reaction employing cyclohexyl reagents **2b** and **3c**.

This kind of differentiation is of particular importance in steroid chemistry. Scheme V illustrates the preferential dithioacetalization of the ketonic group at the 3-position by various methods.[13] In conclusion, the present method is comparable to the Evans' protocol and superior to the conventional method.

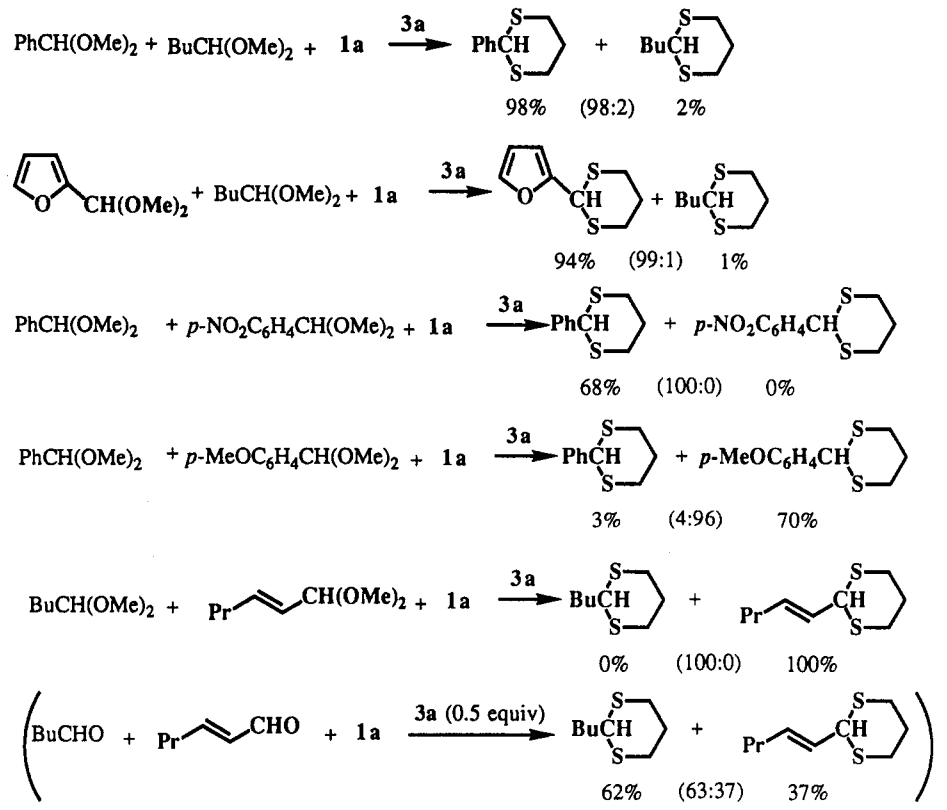
Experimental Section

Melting points were determined in open capillaries and were not corrected. Routine monitoring of reactions was performed with Merck 60 F_{254} silica gel, glass-supported TLC plates. For column chromatography, silica gel 60 (70–230 mesh, E. Merck) was used. IR spectra were measured with a Hitachi 260-10 infrared spectrometer. NMR spectra were recorded on JEOL FX-100 and GSX-400 spectrometers. Mass spectra were obtained

(12) Similar results were reported in an aldol-type reaction of an aldehyde with a ketene silyl acetal in the presence of a europium(III) catalyst: Mikami, K.; Terada, M.; Nakai, T. *J. Org. Chem.* **1991**, *56*, 5456.

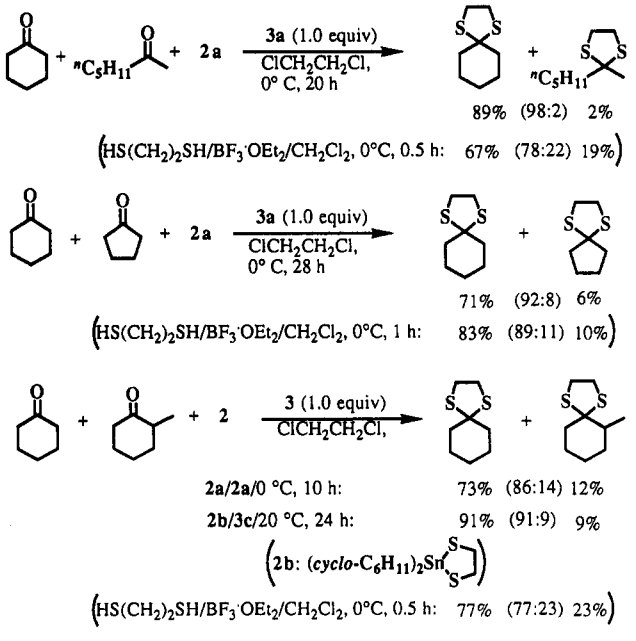
(13) The reaction of 2-cyclohexenone with **2a**/**3a** afforded 3-[(2-mercaptoethyl)thio]cyclohexanone ethylene dithioacetal in 65% yield. See Experimental Section.

Scheme III[a]



[a] **1a** (1.2 equiv) and **3a** (0.3 equiv) were used.

Scheme IV[a]



[a] **2** (1.2 equiv) was used.

with a JEOL JMS-DX 303-HF mass spectrometer using electron impact ionization. GLC analysis was performed on a Shimadzu GC-14A capillary gas chromatograph with a Shimadzu CBP-10 column (0.2 × 25000 mm). Distillations of products were done with a Sibata glass tube oven GTO-250, and boiling points are indicated by an air bath temperature without correction. All reactions were run under an atmosphere of dry nitrogen and in dried solvents. The organic extracts were dried over anhydrous sodium sulfate and concentrated in vacuo. Elemental analyses were performed on a Perkin-Elmer 2400 CHN elemental analyzer.

Starting Materials. 2-Ethyl-2-propenal, (*E*)-2-ethyl-2-butenal, 1,3-propanedithiol, 1,2-ethanedithiol, AgOTf, and 9-methyl-$\Delta^{5(10)}$-octalin-1,6-dione (Wieland–Miescher ketone) were obtained from Aldrich Chemical Co. 4-Androstene-3,17-dione, Δ^4-cholesten-3-one, and progesterone were purchased from Sigma Chemical Co. Bu_2SnCl_2, Me_2SnCl_2, and $(c\text{-}C_6H_{11})_2SnCl_2$ were products of Nitto Kasei Co., and other reagents were obtained from Wako Chemicals. These commercially available reagents were used without purification. The following compounds were prepared: 5α-androstane-3,17-dione [PCC oxidation of (3α,5α)-3-hydroxyandrostane-17-one obtained from Sigma Chemical Co.], geranial and neral [MnO_2 oxidation of geraniol and nerol],[14] $\Delta^{1,9}$-octalone-2,[5d]6-acetoxyhexanal [from hexane-1,6-diol in two steps ((i) Ac_2O, (ii) PCC): IR (neat) 1738 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.68 (m, 6H), 2.04 (s, 3H), 2.46 (t-like, J = 6.83 Hz, 2H), 4.06 (t, J = 6.34 Hz, 2H), 9.76 (t, J = 1.95 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 20.7, 21.5, 25.3, 28.2, 43.5, 63.9, 170.8, 201.8], 6-(tetrahydropyranyloxy)-hexanal [from 6-acetoxy-1-hexanol in 3 steps ((i) DHP-PPTS, (ii) $LiAlH_4$, (iii) PCC): IR (neat) 1720 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.59 (m, 12H), 2.45 (t-like, J = 7.32 Hz, 2H), 3.58 (m, 4H), 4.55 (m, 1H), 9.76 (t, J = 1.95 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 19.4, 21.7, 25.3, 25.7, 29.2, 30.5, 43.6, 62.1, 66.9, 98.6, 202.0], 6-(*tert*-butyldimethylsiloxy)hexanal [from 6-acetoxy-1-hexanol in three steps ((i) *t*-$BuMe_2SiCl$, (ii) $LiAlH_4$, (iii) PCC): IR (neat) 1725 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.02 (s, 6H), 0.87 (s, 9H), 1.47 (m, 6H), 2.41 (t-like, J = 6.83 Hz, 2H), 3.59 (t, J = 6.34 Hz, 2H), 9.74 (t, J = 1.46 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ −5.40, 18.2, 21.8, 25.4, 25.8, 32.4, 43.7, 62.7, 202.1], 6-(*tert*-butyldiphenylsiloxy)hexanal [from 6-acetoxy-1-hexanol in three steps ((i) *t*-$BuPh_2SiCl$, (ii) $LiAlH_4$, (iii) PCC): IR (neat) 1720 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.04 (s, 9H), 1.47 (m, 6H), 2.36 (t-like, J = 6.83 Hz, 2H), 3.65 (t, J = 6.85 Hz, 2H), 7.37 (m, 6H), 7.65 (m, 4H), 9.70 (t, J = 1.95 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 19.0, 21.7, 25.3, 26.7, 32.1, 43.6, 63.4, 127.4, 129.3, 133.9, 135.3, 202.0], 2,2-dibutyl-2-stanna-1,3-dithiolane (**2a**),[15] 2,2-dibutyl-2-stanna-1,3-dithiane (**1a**),[15] and $Bu_2Sn(OTf)_2$ (**3a**).[5a]

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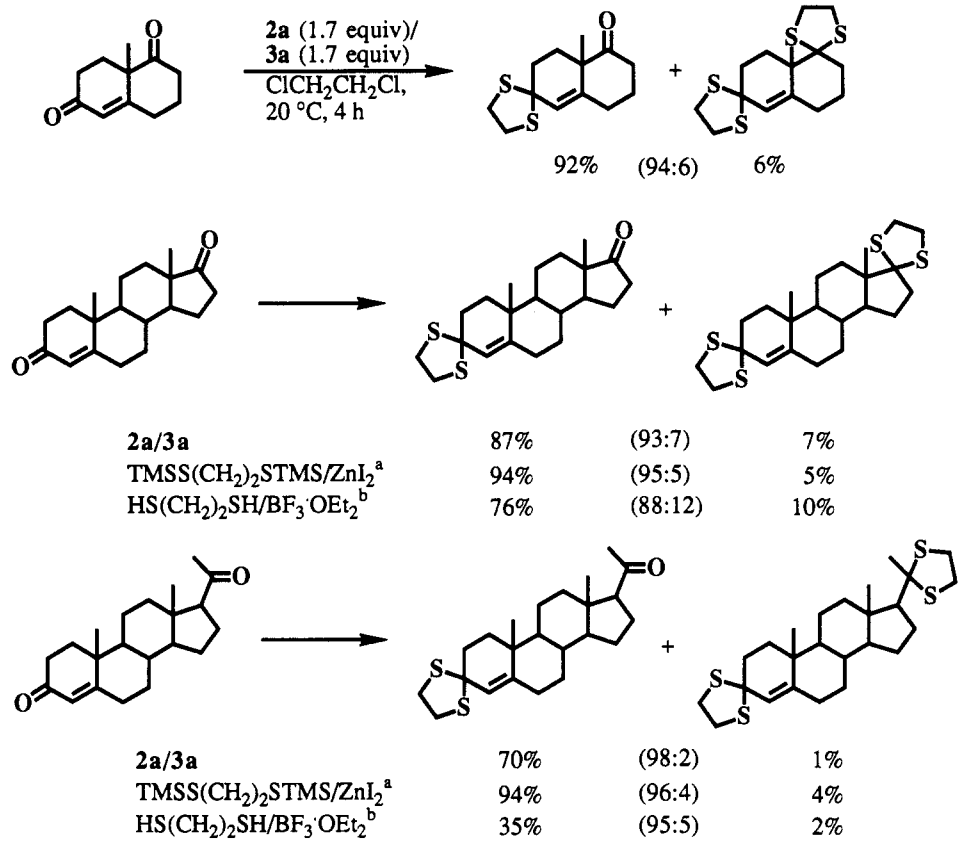
Scheme V



[a] Reference 6. [b] Reference 32.

Dimethyl and ethylene acetals were prepared from the corresponding carbonyl compounds by means of standard methods.[16] $Me_2Sn(OTf)_2$ (**3b**) and $(c\text{-}C_6H_{11})_2Sn(OTf)_2$ (**3c**) were prepared *in situ* from the corresponding R_2SnCl_2 and AgOTf[5a] and were used without purification.

Products. The following compounds were prepared according to the methods described in the literature: 2-phenyl-1,3-dithiane,[17] 2-(4-methoxyphenyl)-1,3-dithiane,[17] 2-(4-nitrophenyl)-1,3-dithiane,[17] 2-(*tert*-butyl)-1,3-dithiane,[18] 2-(2-furyl)-1,3-dithiane,[19] 1-(1,3-dithian-2-yl)-1-propene,[20] 2-butyl-1,3-dithiane,[21] 2-(1,3-dithian-2-yl)-1-butene,[22] 2-(1-naphthyl)-1,3-dithiane,[23] (*E*)-2,6-dimethyl-1-(1,3-dithian-2-yl)-1,5-heptadiene,[24] (*Z*)-2,6-dimethyl-1-(1,3-dithian-2-yl)-1,5-heptadiene,[24] 2-(4-hydroxybutyl)-1,3-dithiane,[25] 2-heptyl-1,3-dithiane,[26] 2,2-dipropyl-1,3-dithiolane,[27] 2-methyl-2-phenyl-1,3-dithiolane,[27] cyclopentanone ethylene dithioacetal,[27] cyclohexanone ethylene dithioacetal,[27] Δ^4-cholestene-3-one ethylene dithioacetal,[28] 2-methyl-2-pentyl-1,3-dithiolane,[29] (*E*)-1-(2-methyl-1,3-dithiolan-2-yl)-2-phenylethene,[30] 9-methyl-$\Delta^{5(10)}$-octalin-1,6-dione 6-ethylene dithioacetal,[31] 9-methyl-$\Delta^{5(10)}$-octalin-1,6-dione 1,6-bis(ethylene dithioacetal),[31] 4-androstene-3,17-dione 3-ethylene dithioacetal,[6,32] 4-androstene-3,17-dione 1,17-bis(ethylene dithioacetal),[6,32] progesterone 3-ethylene dithioacetal,[6,32] and progesterone 3,20-bis(ethylene dithioacetal).[6,32] 2-Methylcyclohexanone ethylene dithioacetal, 1-(1,3-dithian-2-yl)-1-pentene, (1,3-dithian-2-yl)-2-pentene, 2-butyl-2-methyl-1,3-dithiane, and 2-(5-hydroxypentan-1-yl)-1,3-dithiane were prepared from the corresponding carbonyl compounds and dithiols under standard conditions (BF_3·OEt_2/CH_2Cl_2). Physical data of these compounds are given below. **2-Methylcyclohexanone ethylene dithioacetal**: bp 100 °C (5 mmHg); ^{1}H NMR ($CDCl_3$) δ 1.05 (d, J = 6.59 Hz, 3 H), 1.08–1.28 (m, 2H), 1.40–1.90 (m, 6H), 2.10–2.20 (m, 1H), 3.12–3.22 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 18.1, 24.8, 25.9, 34.1, 38.6, 39.2, 42.8, 44.7, 74.5; MS (*m/z*) 188 (M^+); HRMS calcd for $C_9H_{16}S_2$ (M^+) 188.0694, found 188.0547. Anal. Calcd for $C_9H_{16}S_2$: C, 57.39; H, 8.57. Found: C, 57.2; H, 8.43. **1-(1,3-Dithian-2-yl)-1-pentene** (*E*/*Z* = 88:12): bp 150 °C (7 mmHg); ^{1}H NMR ($CDCl_3$) δ 0.89 (t, J = 7.45 Hz, 3H × 88/100), 0.93 (t, J = 7.26 Hz, 3H × 12/100), 1.34–1.48 (m, 2H), 1.77–2.19 (m, 4H), 2.78–3.02 (m, 4H), 4.63 (d, J = 7.57 Hz, 1H × 88/100), 4.95 (d, J = 9.89 Hz, 1H × 12/100), 5.38 (t-like, J = 10.0 Hz, 1H × 12/100), 5.52 (dd, J = 7.57, 15.3 Hz, 1H × 88/100), 5.86 (dt, J = 6.04, 15.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) (major) δ 13.4, 21.8, 25.0, 30.2, 34.0, 47.5, 126.5, 134.9 (minor) δ 13.6, 22.4, 24.7, 29.6, 30.1, 43.0, 125.7, 134.2; MS (*m/z*) 188 (M^+); HRMS calcd for $C_9H_{16}S_2$ (M^+) 188.0684, found 188.0636. Anal. Calcd for $C_9H_{16}S_2$: C, 57.39; H, 8.57. Found: C, 57.30; H, 8.52. **3-(1,3-Dithian-2-yl)-2-pentene** (*E*/*Z* = 89:11): bp 100 °C (5 mmHg); ^{1}H NMR ($CDCl_3$) δ 1.05 (t, J = 7.33 Hz, 3H × 89/100), 1.06 (t, J = 7.33 Hz, 3H × 11/100), 1.66 (d, J = 6.96 Hz, 3H), 1.75–2.15 (m, 4H), 2.20 (q, J = 7.33 Hz, 2H), 2.80–3.00 (m, 4H), 4.53 (s, 1H × 89/100), 5.06 (s, 1H × 11/100), 5.39 (q, J = 6.96 Hz, 1H × 11/100), 5.74 (q, J = 6.96 Hz, 1H × 89/100); ^{13}C NMR ($CDCl_3$) (major) δ 13.1, 13.4, 22.7, 25.3, 31.8, 52.8, 124.2, 138.7; (minor) δ 12.9, 13.6, 26.8, 31.5, 49.4, 122.4, 138.1; MS (*m/z*) 188 (M^+); HRMS

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calcd for $C_9H_{16}S_2$ (M^+) 188.0694, found 188.0608. Anal. Calcd for $C_9H_{16}S_2$: C, 57.39; H, 8.57. Found: C, 57.42; H, 8.60. **2-Butyl-2-methyl-1,3-dithiane**: bp 130 °C (5 mmHg); ^1H NMR ($CDCl_3$) δ 0.93 (t, J = 7.15 Hz, 3H), 1.2–2.1 (m, 8H), 1.62 (s, 3H), 2.83 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 13.9, 22.7, 25.3, 26.3, 26.5, 27.6, 41.3, 49.1, 77.4; MS (m/z) 190 (M^+); HRMS calcd for $C_9H_{18}S_2$ (M^+) 190.0850, found 190.0818. Anal. Calcd for $C_9H_{18}S_2$: C, 56.78; H, 9.53. Found: C, 56.49; H, 9.20. **2-(5-Hydroxypentan-1-yl)-1,3-dithiane**: bp 200 °C (7 mmHg); IR (neat) 3350 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.59 (m, 10H), 2.83 (m, 4H), 3.63 (t, J = 6.34 Hz, 2H), 4.05 (t, J = 6.59 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 25.1, 25.8, 26.1, 30.2, 32.2, 35.1, 47.2, 62.4; MS (m/z) 206 (M^+). Anal. Calcd for $C_9H_{18}OS_2$: C, 52.38; H, 8.79. Found: C, 52.60; H, 8.71.

Preparation of 2,2-Dimethyl-2-stanna-1,3-dithiane (1b). A mixture of Me_2SnCl_2 (11.0 g, 50 mmol), 1,3-propanedithiol (5.02 mL, 50 mmol), Et_3N (13 mL, 100 mmol), and CH_2Cl_2 (200 mL) was stirred at rt for 24 h. The resulting mixture was diluted with CH_2Cl_2 (100 mL) and washed with H_2O (100 mL × 2). The organic layer was dried and evaporated to afford an oil. Bulb-to-bulb distillation of this oil gave the title compound (8.2 g, 64%): bp 170 °C (18 mmHg); ^1H NMR ($CDCl_3$) δ 0.81 (s, 6H), 1.89 (m, 2H), 2.93 (t-like, J = 6.34 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ −1.02, 24.5, 29.6. Anal. Calcd for $C_5H_{12}S_2Sn$: C, 23.55; H, 4.75. Found: C, 23.71; H, 4.70.

In a similar way, 2,2-dicyclohexyl-2-stanna-1,3-dithiane and 2,2-dicyclohexyl-2-stanna-1,3-dithiolane were prepared. **2,2-Dicyclohexyl-2-stanna-1,3-dithiane (1c)** (77% yield): bp 210 °C (0.8 mmHg); mp 104–110 °C; ^1H NMR ($CDCl_3$) δ 1.72 (m, 24H), 2.95 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 24.1, 26.4, 28.4, 29.6, 31.0, 36.7. Anal. Calcd for $C_{15}H_{28}S_2Sn$: C, 46.05; H, 7.21. Found: C, 45.86; H, 7.10. **2,2-Dicyclohexyl-2-stanna-1,3-dithiolane (2b)** (83% yield): bp 210 °C (0.9 mmHg); ^1H NMR ($CDCl_3$) δ 1.22–2.24 (m, 22H), 3.00 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 26.3, 28.3, 30.9, 36.1, 36.6. Anal. Calcd for $C_{14}H_{26}S_2Sn$: C, 44.58; H, 6.95. Found: C, 44.78; H, 7.03.

General Procedure for the Preparation of 1,3-Dithianes. Reaction of Furfural with 2,2-Dibutyl-2-stanna-1,3-dithiane in the Presence of $Bu_2Sn(OTf)_2$. A mixture of furfural (48 mg, 0.5 mmol), 2,2-dibutyl-2-stanna-1,3-dithiane (203 mg, 0.6 mmol), $Bu_2Sn(OTf)_2$ (80 mg, 0.15 mmol), and $ClCH_2CH_2Cl$ (4 mL) was stirred at 35 °C for 20 h. GLC analysis of the reaction mixture indicated the formation of the corresponding 1,3-dithiane in 100% yield relative to n-$C_{15}H_{32}$ as an internal standard. 1 N NaOH (1 mL) was added to the reaction mixture, which was then diluted with CH_2Cl_2 (50 mL). The organic layer was washed with 1 N NaOH and H_2O. Drying and evaporation left an oil, which was purified by column chromatography on silica gel (95:5 hexane–ethyl acetate) to give pure 2-(2-furfuryl)-1,3-dithiane (79 mg, 85%) identical with an authentic specimen.[19]

Other 1,3-dithianes were prepared analogously. The spectroscopic and analytical data of new compounds are as follows: **2-(5-Acetoxypentan-1-yl)-1,3-dithiane**: bp 180 °C (3 mmHg); IR (neat) 1735 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.67 (m, 10H), 2.03 (s, 3H), 2.82 (m, 4H), 4.04 (t-like, J = 6.59 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 20.7, 25.5, 25.8, 26.1, 28.2, 30.2, 35.2, 47.3, 64.1, 170.7; MS (m/z) 248 (M^+); HRMS calcd for $C_{11}H_{20}O_2S_2$ (M^+) 248.090, found 248.087. Anal. Calcd for $C_{11}H_{20}O_2S_2$: C, 53.19; H, 8.11. Found: C, 53.10; H, 8.15. **2-[5-(Tetrahydropyranyloxy)pentan-1-yl]-1,3-dithiane**: bp 200 °C (3 mmHg); ^1H NMR ($CDCl_3$) δ 1.34–2.18 (m, 16H), 2.76–2.94 (m, 2H), 3.34–3.55 (m, 2H), 3.69–3.91 (m, 2H), 4.04 (t, J = 6.89 Hz, 1H), 4.57 (m, 1H), ^{13}C NMR ($CDCl_3$) δ 19.3, 25.2, 25.6, 25.7, 26.1, 29.2, 30.1, 30.4, 35.1, 47.2, 61.9, 67.0, 98.4; MS (m/z) 206 (M^+ − THP); HRMS calcd for $C_9H_{17}OS_2$ (M^+ − THP) 206.0748, found 206.0778. Anal. Calcd for $C_{14}H_{26}O_2S_2$: C, 57.89; H, 9.02. Found: C, 57.60; H, 9.23. **2-[5-(*tert*-Butyldimethylsiloxy)pentan-1-yl]-1,3-dithiane**: bp 180 °C (5 mmHg); ^1H NMR ($CDCl_3$) δ 0.04 (s, 6H), 0.88 (s, 9H), 1.53 (m, 10H), 2.81 (m, 4H), 3.59 (t, J = 6.34 Hz, 2H), 4.04 (t, J = 6.59 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ −5.36, 18.2, 25.3, 25.8, 25.9, 26.3, 30.3, 32.4, 35.3, 47.5, 62.8; MS (m/z) 305 (M^+ − CH_3); HRMS calcd for $C_{11}H_{23}OS_2Si$ (M^+ − t-C_4H_9) 263.0960, found 263.0944. Anal. Calcd for $C_{15}H_{32}OS_2Si$: C, 56.19; H, 10.06. Found: C, 56.30; H, 10.30. **2-[5-(*tert*-Butyldiphenylsiloxy)pentan-1-yl]-1,3-dithiane**: ^1H NMR ($CDCl_3$) δ 1.04 (s, 9H), 1.46 (m, 10H), 2.77 (m, 4H), 3.65 (t, J = 5.85 Hz, 2H), 4.01 (t, J = 6.59 Hz, 1H), 7.40 (m, 6H), 7.65 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 19.0, 25.3, 25.9, 26.4, 26.7, 30.2, 32.1, 35.2, 63.5, 127.4, 129.2, 133.9, 135.3; MS (m/z) 387 (M^+ − t-C_4H_9); HRMS calcd for $C_{21}H_{27}OS_2Si$ (M^+ − t-C_4H_9) 387.1273, found 387.1248. Anal. Calcd for $C_{25}H_{36}OS_2Si$: C, 67.51; H, 8.16. Found: C, 67.71; H, 8.00.

Reaction of 6-(Tetrahydropyranyloxy)hexanal and 1,3-Propanedithiol in the Presence of BF_3·OEt_2. A mixture of 6-(tetrahydropyranyloxy)hexanal (81 mg, 0.41 mmol), 1,3-propanedithiol (49 mg, 0.45 mmol), BF_3·OEt_2 (5.7 mg, 0.04 mmol), and CH_2Cl_2 (3 mL) was stirred at 0 °C for 3 h. After workup and column chromatography, 2-(5-hydroxypentan-1-yl)-1,3-dithiane (85 mg, 100%) was obtained. Other reactions in the presence of BF_3·OEt_2 were carried out analogously.

A Typical Procedure for the Competition Reactions of Aldehydes (or Acetals) and Ketones (or Ketals) with 2,2-Dibutyl-2-stanna-1,3-dithiane in the Presence of $R_2Sn(OTf)_2$. Competition Reaction of Pentanal and 2-Hexanone. A mixture of pentanal (43 mg, 0.5 mmol), 2-hexanone (50 mg, 0.5 mmol), 2,2-dibutyl-2-stanna-1,3-dithiane (203 mg, 0.6 mmol), $Bu_2Sn(OTf)_2$ (81 mg, 0.15 mmol), and $ClCH_2CH_2Cl$ (4 mL) was stirred at 0 °C for 4 h. GLC analysis of the reaction mixture indicated the formation of 2-butyl-1,3-dithiane in 74% yield and complete recovery of 2-hexanone relative to n-$C_{10}H_{22}$ as an internal standard. No 2-butyl-2-methyl-1,3-dithiane was formed.

Competition Reaction of Benzaldehyde and Pentanal. 2,2-Dibutyl-2-stanna-1,3-dithiane–$Bu_2Sn(OTf)_2$ Method. A mixture of benzaldehyde (53 mg, 0.5 mmol), pentanal (43 mg, 0.5 mmol), 2,2-dibutyl-2-stanna-1,3-dithiane (170 mg, 0.5 mmol), $Bu_2Sn(OTf)_2$ (133 mg, 0.25 mmol), and $ClCH_2CH_2Cl$ (4 mL) was stirred at 0 °C for 1 h. GLC analysis of the reaction mixture indicated the formation of 2-butyl-1,3-dithiane (90%) and 2-phenyl-1,3-dithiane (8.5%) in a 91:9 ratio.

The 1,3-Propanedithiol–BF_3·OEt_2 Method. Upon treatment of benzaldehyde (53 mg, 0.5 mmol) and pentanal (43 mg, 0.5 mmol) with 1,3-propanedithiol (65 mg, 0.6 mmol) and BF_3·OEt_2 (35 mg, 0.25 mmol) in $ClCH_2CH_2Cl$ (4 mL) at 0 °C for 1 h, an oil was obtained. GLC analysis of this oil showed that the crude product consisted of 2-butyl-1,3-dithiane (76%) and 2-phenyl-1,3-dithiane (24%) in a 76:24 ratio.

The 2,2-Dibutyl-2-stanna-1,3-dithiane–BF_3·OEt_2 Method. A mixture of benzaldehyde (53 mg, 0.5 mmol) and pentanal (43 mg, 0.5 mmol) in $ClCH_2CH_2Cl$ (4 mL) was treated with 2,2-dibutyl-2-stanna-1,3-dithiane (203 mg, 0.6 mmol) and BF_3·OEt_2 (35 mg, 0.25 mmol) at 0 °C for 1 h. GLC analysis of the crude product indicated that 2-butyl-1,3-dithiane (77%) and 2-phenyl-1,3-dithiane (21%) were formed in a 79:21 ratio.

The 1,3-Propanedithiol–$Bu_2Sn(OTf)_2$ Method. Upon treatment of benzaldehyde (53 mg, 0.5 mmol) and pentanal (43 mg, 0.5 mmol) in $ClCH_2CH_2Cl$ (4 mL) with 1,3-propanedithiol (54 mg, 0.5 mmol) and $Bu_2Sn(OTf)_2$ (135 mg, 0.25 mmol) at 0 °C for 1 h, 2-butyl-1,3-dithiane (71%) and 2-phenyl-1,3-dithiane (29%) were obtained in a 71:29 ratio.

Competition Reaction of Pentanal and 2,2-Dimethylpropanal. 2,2-Dicyclohexyl-2-stanna-1,3-dithiane–$(c\text{-}C_6H_{11})_2Sn(OTf)_2$ Method. In $ClCH_2CH_2Cl$. From pentanal (43 mg, 0.5 mmol), 2,2-dimethylpropanal (43 mg, 0.5 mmol), 2,2-dicyclohexyl-2-stanna-1,3-dithiane (235 mg, 0.6 mmol), $(c\text{-}C_6H_{11})_2Sn(OTf)_2$ [prepared from $(c\text{-}C_6H_{11})_2SnCl_2$ (89 mg, 0.25 mmol), and AgOTf (128 mg, 0.5 mmol) in $ClCH_2CH_2Cl$ (1 mL)], and $ClCH_2CH_2Cl$ (3 mL) at 0 °C for 0.5 h, an oil was obtained. GLC analysis showed that the crude product consisted of 2-butyl-1,3-dithiane (89%) and 2-(*tert*-butyl)-1,3-dithiane (11%) in a 89:11 ratio.

In CH_3CN. In a similar way, a mixture of pentanal (43 mg, 0.5 mmol) and 2,2-dimethylpropanal (43 mg, 0.5 mmol) was treated with 2,2-dicyclohexyl-2-stanna-1,3-dithiane (235 mg, 0.6 mmol), $(c\text{-}C_6H_{11})_2Sn(OTf)_2$ [prepared from $(c\text{-}C_6H_{11})_2SnCl_2$ (89 mg, 0.25 mmol) and AgOTf (128 mg, 0.5 mmol) in CH_3CN (1 mL)], and CH_3CN (3 mL) at 0 °C for 1 h. GLC analysis of the reaction mixture indicated the formation of 2-butyl-1,3-dithiane (86%) and 2-*tert*-butyl-1,3-dithiane (6.7%) in a 93:7 ratio.

General Procedure for the Preparation of 1,3-Dithiolanes. Reaction of $\Delta^{1,9}$-Octalone-2 with 2,2-Dibutyl-2-stanna-1,3-dithiolane in the Presence of $Bu_2Sn(OTf)_2$. A mixture of $\Delta^{1,9}$-octalone-2 (45 mg, 0.3 mmol), 2,2-dibutyl-2-stanna-1,3-dithiolane (166 mg, 0.51 mmol), $Bu_2Sn(OTf)_2$ (271 mg, 0.51 mmol), and $ClCH_2CH_2Cl$ (2 mL) was stirred at 20 °C for 20 h. The

reaction mixture was diluted with ether, and the resulting organic layer was washed with 1 N NaOH and saturated aqueous NaCl. Drying and evaporation left an oil. Column chromatography of this oil (50:50 hexane–benzene) gave $\Delta^{1,9}$-octalone-2 ethylene dithioacetal (67 mg, 99%). No products of isomerization of the double bond could be obtained: bp 150 °C (4 mmHg); ^{1}H NMR ($CDCl_3$) δ 1.04 (qd, J = 2.93, 12.4 Hz, 1H), 1.20–1.55 (m, 3H), 1.70–1.85 (m, 3H), 1.88–2.10 (m, 4H), 2.15–2.25 (m, 2H), 3.21–3.45 (m, 4H), 5.55 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 25.9, 27.2, 30.1, 34.5, 34.8, 36.3, 39.4, 39.7, 40.0, 65.7, 124.2, 142.3; MS (m/z) 226 (M^+); HRMS calcd for $C_{12}H_{18}S_2$ (M^+) 226.0850, found 226.0820. Anal. Calcd for $C_{12}H_{18}S_2$: C, 63.66; H, 8.01. Found: C, 63.37; H, 8.21.

Other reactions were conducted analogously. Spectroscopic and analytical data of a new compound are as follows. **5α-Androstane-3,17-dione 3-ethylene dithioacetal**: mp 205–206 °C; ^{1}H NMR ($CDCl_3$) δ 0.80 (m, 1H), 0.83 (s, 3H), 0.85 (s, 3H), 1.02 (qd, J = 4.77, 12.0 Hz, 1 H), 1.20–1.80 (m, 14H), 1.90–2.15 (m, 5H), 2.43 (dd, J = 8.43, 19.4 Hz, 1H), 3.25–3.33 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 11.8, 13.7, 20.2, 21.7, 27.9, 30.5, 31.4, 34.9, 35.4, 35.8, 37.8, 38.1, 38.71, 38.79, 45.0, 46.3, 47.7, 51.3, 54.0, 68.8, 221.2; MS (m/z) 364 (M^+); HRMS calcd for $C_{21}H_{32}OS_2$ (M^+) 364.1895, found 364.1988. Anal. Calcd for $C_{21}H_{32}OS_2$: C, 69.18; H, 8.85. Found: C, 69.10; H, 8.65. Relevant data of known 1,3-dithiolanes are complied in the supplementary material.

A Typical Procedure for Differentiation between Ketones in 1,3-Dithiolane Synthesis. Competitive Reaction of Cyclohexanone and 2-Heptanone. 2,2-Dibutyl-2-stanna-1,3-dithiolane in the Presence of $Bu_2Sn(OTf)_2$. A mixture of cyclohexanone (49 mg, 0.5 mmol), 2-heptanone (57 mg, 0.5 mmol), 2,2-dibutyl-2-stanna-1,3-dithiolane (195 mg, 0.6 mmol), $Bu_2Sn(OTf)_2$ (265 mg, 0.5 mmol), and $ClCH_2CH_2Cl$ (3 mL) was stirred at 0 °C for 20 h. GLC analysis of the reaction mixture indicated the formation of cyclohexanone ethylene dithioacetal (89%) and 2-methyl-2-pentyl-1,3-dithiolane (2%) in a 97:3 ratio.

1,2-Ethanedithiol in the Presence of BF_3·OEt_2. A mixture of cyclohexanone (49 mg, 0.5 mmol), 2-heptanone (57 mg, 0.5 mmol), and CH_2Cl_2 (3 mL) was treated with 1,2-ethanedithiol (57 mg, 0.6 mmol) in the presence of BF_3·OEt_2 (36 mg, 0.25 mmol) at 0 °C for 0.5 h. Cyclohexanone ethylene dithioacetal (67%) and 2-methyl-2-pentyl-1,3-dithiolane (19%) were produced in a 78:22 ratio.

Reaction of 2-Cyclohexenone with 2,2-Dibutyl-2-stanna-1,3-dithiolane in the Presence of $Bu_2Sn(OTf)_2$. A mixture of 2-cyclohexenone (29 mg, 0.3 mmol), 2,2-dibutyl-2-stanna-1,3-dithiolane (166 mg, 0.51 mmol), $Bu_2Sn(OTf)_2$ (271 mg, 0.51 mmol), and $ClCH_2CH_2Cl$ (2 mL) was stirred at 20 °C for 3 h. Workup and column chromatography provided 3-[(2-mercaptoethyl)thio]-cyclohexanone ethylene dithioacetal (52 mg, 65%): bp 200 °C (4 mmHg); ^{1}H NMR ($CDCl_3$) δ 1.25 (m, 1H), 1.62 (m, 1H), 1.73 (t, J = 7.69 Hz, 1 H), 1.89 (m, 3H), 1.98 (d-like, J = 12.8 Hz, 1H), 2.12 (d-like, J = 13.1 Hz, 1H), 2.40 (d-like, J = 10.2 Hz, 1H), 2.80 (m, 5H), 3.38 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 25.0, 25.9, 32.3, 34.2, 38.0, 39.0, 41.6, 42.3, 49.5, 67.9; MS (m/z) 266 (M^+); HRMS calcd for $C_{10}H_{18}S_4$ (M^+) 266.0291, found 266.0223. Anal. Calcd for $C_{10}H_{18}S_4$: C, 45.07; H, 6.81. Found: C, 45.32; H, 6.71.

Supplementary Material Available: Experimental methods (4 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.