Lewis Acid-Promoted Deoxygenative Di[*β*,*β*-bis(ethylthio)]vinylation of Aldehydes with Trimethylsilylketene Bis(ethylthio)acetal

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Silylketene dithioacetal **1** reacted with aldehydes **2a**−**o**, **14**, or cinnamaldehyde (**11**) in the presence of Lewis acid to give deoxygenative divinylation products, 3-substituted 1,4-pentadienes **3a**−**o**, **15**, or 5-phenyl-1,3,6-heptatriene **13b**, in good to moderate yields. Similar reaction with 2-aminobenzaldehyde (**16**) or salicylaldehyde (**17**) produced quinoline **19** or chroman **20** in 40−58% yield. Treatment of **1** with α-diketones **22a**−**c** or α-ketoester **24** led to tetrasubstituted furans **23a**−**c** or allylic alcohol **25**, respectively, in rather low yields. The formation mechanisms of these products are discussed.

The reactions of allylsilanes and vinylsilanes with electrophiles have been extensively studied due to their synthetic usefulness.[1] In the presence of Lewis acid or fluoride anion, allylsilanes reacted with electrophiles such as ketones and aldehydes to afford homoallyl alcohols.[2] On the other hand, the reaction of vinylsilanes with aldehydes or ketones is currently hampered by limited substrate generality, where the use of special vinylsilanes or reactive carbonyl compounds is indispensable.[1e,i] We have recently reported the first synthesis of α-silyl- and α-stannyl-*β*-heteroatom-substituted vinylphosphonates and their functional group transformations at the α-position.[3] In connection with our exploration of new synthetic routes for introduction of a functionalized vinyl group, we became interested in the synthesis and synthetic utilization of silylketene dithioacetals, which are a new class of vinylsilanes and are expected to show various reactivities attributable to vinylsilanes,[1] ketene dithioacetals,[4] heteroatom-substituted olefins,[5] etc. Despite a hopeful prospect of developing synthetic utility of silylketene dithioacetals as high reactive vinylsilanes, their chemistry has been scarcely studied.[6,7] Accordingly, we have begun to investigate the reactivity of silylketene dithioacetal toward carbonyl compounds. We found an unprecedented addition of silylketene dithioacetal **1** to aldehydes in the presence of Lewis acid. We report here a novel di[*β*,*β*-bis(ethylthio)]vinylation of aldehydes with **1** giving tetrakis(ethylthio)-1,4-pentadiene, and also new synthesis of heterocyclic compounds from **1** and *o*-NH_2 or OH-substituted benzaldehydes or α-diketones.

Results and Discussion

Deoxygenative Divinylation of Aldehydes with Silylketene Dithioacetal. To compare the reactivities of silylketene dithioacetal **1**[8] toward carbonyl compounds with that of vinylsilane, the reaction of **1** (1 equiv) with benzaldehyde (**2a**) (1 equiv) was carried out in CH_2Cl_2 in the presence of $BF_3{\cdot}OEt_2$ (1 equiv) at −78 °C for 1 h. No allylic alcohol **4** was obtained, and unprecedented deoxygenative addition[9] of **1** to **2a** proceeded to give 1,1,5,5-tetrakis(ethylthio)-3-phenyl-1,4-pentadiene (**3a**) in 71% yield (entry 1 in Table 1) (Scheme 1). Hosomi and co-workers reported that the reaction of a silylketene dithioacetal with aromatic aldehydes in the presence of $BF_3{\cdot}OEt_2$ or $TiCl_4$ gave allylic alcohols **4**,[6] whereas we could not obtain the corresponding allylic alcohols at all.

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(1) See, for examples: (a) Fleming, I.; Barbero, A.; Walter, D. *Chem. Rev*. **1997**, *97*, 2063. (b) Langkopf, E.; Schinzer, D. *Chem. Rev*. **1995**, *95*, 1375. (c) Masse, C. E.; Panek, J. S. *Chem. Rev*. **1995**, *95*, 1293. (d) Hosomi, A. *Acc. Chem. Res*. **1988**, *21*, 200. (e) Overman, L. E.; Blumenkopf, T. A. *Chem. Rev*. **1986**, *86*, 857. (f) Sakurai, H. *Pure Appl. Chem*. **1982**, *54*, 1. (g) Chan, T. H.; Fleming, I. *Synthesis* **1979**, 761. (h) Panek, J. S. *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon Press: Oxford, 1991; Vol. 1, Chapter 2.5. (i) Fleming, I. *Organic Reactions*; Kende, A. S., Ed.; John Wiley & Sons: New York, 1989; Vol. 37, 57. (j) Colvin, E. W. *Silicon in Organic Synthesis*; Butterworth: London, 1981; Chapter 7, 9.

(2) (a) Hosomi, A.; Sakurai, H. *Tetrahedron Lett.* **1976**, *17*, 1295. (b) Hosomi, A.; Shirahata, A.; Sakurai, H. *Tetrahedron Lett*. **1978**, *19*, 3043.

(3) Kouno, R.; Okauchi, T.; Nakamura, M.; Ichikawa, J.; Minami, T. *J. Org. Chem*. **1998**, *63*, 6239.

(4) For reviews of ketene dithioacetal, see: (a) Kolb, M. *Synthesis* **1990**, 171. (b) Junjappa, H.; Ila, H.; Asokan, C. V. *Tetrahedron* **1990**, *46*, 5423.

(5) (a) Knight, D. W. *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon Press: Oxford, 1991; Vol. 3, Chapter 1.6. (b) Braun, M. *Angew. Chem., Int. Ed. Engl*. **1998**, *37*, 430. (c) Kauffmann, T. *Angew. Chem., Int. Ed. Engl*. **1982**, *21*, 410.

(6) Tominaga, Y.; Matuoka, Y.; Kamio, C.; Hosomi, A. *Chem. Pharm. Bull*. **1989**, *37*, 3168.

(7) For the synthesis of α-substituted silylketene dithioacetals, see: (a) Chamberlin, A. R.; Nguyen, H. *J. Org. Chem*. **1986**, *51*, 940. (b) Yamamoto, M.; Takemori, T.; Iwasa, S.; Kohmoto, S.; Yamada, K. *J. Org. Chem*. **1989**, *54*, 1757.

(8) The synthetic method of silylketene dithioacetal is described in the Supporting Information. A similar synthesis of a silylketene dithioacetal was previously reported, see: ref 6.

(9) For example, deoxygenative addition of indoles with carbonyl compounds is known to produce bisindolylmethanes; see: Babu, G.; Sridhar, N.; Perumal, P. T. *Synth. Commun*. **2000**, *30*, 1609 and references therein. For deoxygenation of carbonyl compounds by metal reagents, see: Xi, Z.; Li, P. *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 2950 and references there-in.

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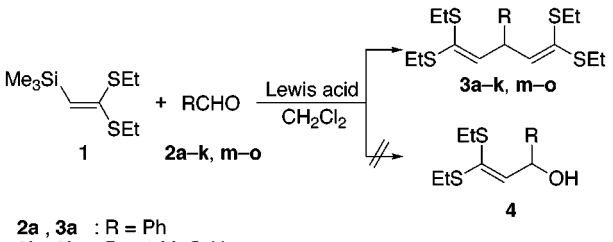
Table 1. Lewis Acid-Promoted Reaction of Silylketene Dithioacetal 1 with Aldehydes 2[a]

entry	ECHO (equiv)	Lewis acid (equiv)	time, h	product[b] (yield, %)
1	**2a** (1.0)	$BF_3{\cdot}OEt_2$ (1.0)	1.0	**3a** (71)
2	**2a** (0.5)	$BF_3{\cdot}OEt_2$ (0.5)	1.0	**3a** (71)
3	**2a** (0.5)	$BF_3{\cdot}OEt_2$ (0.1)	1.0	**3a** (70)
4	**2a** (1.0)	$TiCl_4$ (1.0)	1.0	**3a** (63)
5	**2a** (0.5)	$TiCl_4$ (0.5)	1.0	**3a** (56)
6	**2a** (0.5)	$TiCl_4$ (0.1)	1.0	**3a** (60)
7	**2a** (1.0)	TMSOTf (1.0)	1.0	**3a** (58)
8	**2a** (0.5)	TMSOTf (0.5)	1.0	**3a** (58)
9	**2a** (0.5)	TMSOTf (0.1)	1.0	**3a** (58)
10	**2b** (0.5)	$BF_3{\cdot}OEt_2$ (0.5)	1.0	**3b** (70)
11	**2c** (0.5)	$BF_3{\cdot}OEt_2$ (0.5)	2.0	**3c** (52)
12	**2d** (0.5)	$BF_3{\cdot}OEt_2$ (0.5)	1.0	**3d** (60)
13	**2e** (0.5)	$BF_3{\cdot}OEt_2$ (0.5)	1.0	**3e** (78)
14	**2f** (1.0)	$BF_3{\cdot}OEt_2$ (1.0)	1.0	**3f** (88)
15	**2g** (1.0)	$BF_3{\cdot}OEt_2$ (1.0)	1.0	**3g** (87)
16	**2h** (0.5)	$BF_3{\cdot}OEt_2$ (0.5)	1.0	**3h** (60−70)
17	**2i** (1.0)	$BF_3{\cdot}OEt_2$ (1.0)	1.0	**3i** (60)
18	**2j** (0.5)	$BF_3{\cdot}OEt_2$ (0.5)	1.5	**3j** (58)
19	**2k** (0.5)	$BF_3{\cdot}OEt_2$ (0.5)	1.5	**3k** (75)
20	**2l** (0.25)	$BF_3{\cdot}OEt_2$ (0.5)	1.0	**3l** (64)
21	**2m** (1.0)	$EtAlCl_2$ (1.0)	2.0	**3m** (38)
22	**2n** (1.0)	$EtAlCl_2$ (1.0)	1.0	**3n** (42)
23	**2o** (1.0)	$EtAlCl_2$ (1.0)	1.0	**3o** (44)

[a] All reactions were carried out in CH_2Cl_2 at −78 °C. [b] Isolated yield. Yields were based on silylketene dithioacetal **1**.

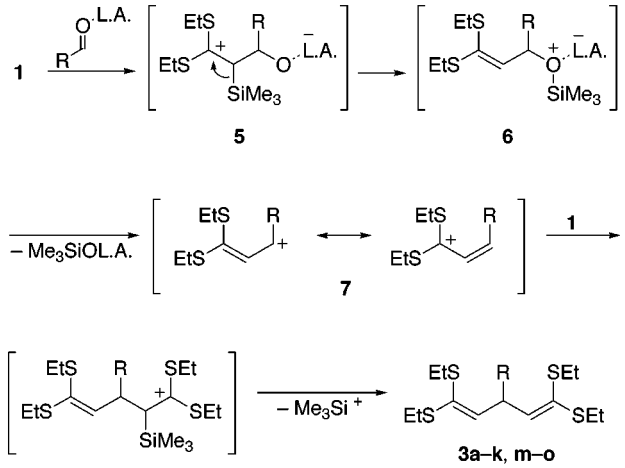
Scheme 1



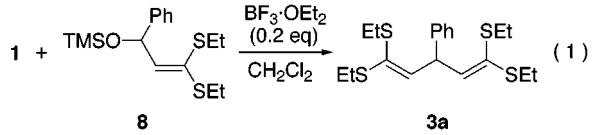
2a , 3a : R = Ph
2b , 3b : R = 4-MeC_6H_4
2c , 3c : R = 2-MeC_6H_4
2d , 3d : R = 4-$MeOC_6H_4$
2e , 3e : R = 4-ClC_6H_4
2f , 3f : R = 4-$NO_2C_6H_4$
2g , 3g : R = 4-CNC_6H_4
2h , 3h : R = 1-Naphthyl
2i , 3i : R = 2-PhC_6H_4
2j , 3j : R = 2-Furyl
2k , 3k : R = 2-Thienyl
2m, 3m : R = $Ph(CH_2)_2$
2n , 3n : R = $CH_3(CH_2)_5$
2o , 3o : R = $(CH_3)_2CH$

So we next examined the influence of the molar ratio of **1** to **2a** and $BF_3{\cdot}OEt_2$ upon the product and the product yield. The silylketene dithioacetal **1** was treated with a 0.5 molar amount of **2a** and $BF_3{\cdot}OEt_2$ to produce only **3a** in the same yield (71%) (entry 2). Even when a catalytic amount of $BF_3{\cdot}OEt_2$ was used, **3a** was obtained in a similar yield (70%) (entry 3). These results have indicated that the reaction of **1** with **2a** led to the formation of only the deoxygenative divinylation product **3a** regardless of the molar amount of $BF_3{\cdot}OEt_2$ used. The use of $TiCl_4$ or trimethylsilyl trifluoromethanesulfonate (TMSOTf), instead of $BF_3{\cdot}OEt_2$, showed a similar trend in the yield of **3a**, although the yield slightly decreased (58−63% yield) (entries 4−9). No reaction between **1** and **2a** proceeded without Lewis acid. On the basis of these results, the formation of **3a** is rationalized as follows: Lewis acid-activated benzaldehyde underwent the addition of the electron rich silylketene dithioacetal **1** to give the cation **5** stabilized by both a β-trimethylsilyl (TMS) group[10] and two α-ethylthio groups,[11] followed by elimination of the TMS cation resulting in allyloxonium cation **6**, C−O bond cleavage producing allylic cation **7**.[12] The subsequent reaction with another **1** led to the product **3a** with generation of the TMS cation (Scheme 2).

Scheme 2



To confirm the above-mentioned mechanism, 1,1-bis(ethylthio)-3-phenyl-3-trimethylsiloxy-1-propene (**8**), prepared independently from the corresponding allylic alcohol[13] and chlorotrimethylsilane, was allowed to react with **1** in the presence of a catalytic amount of $BF_3{\cdot}OEt_2$ (0.2 equiv) to give the expected **3a** in 55% yield (eq 1). This experimental result evidently supports the mechanism shown in Scheme 2.



Furthermore, the role of the alkylthio group in this deoxygenative divinylation was investigated. Treatment of benzaldehyde (**2a**) with methyl 2-(trimethylsilyl)vinyl sulfide (**9**)[14] instead of **1** under the same conditions led to only an uncharacterizable mixture (eq 2). This result clearly indicates that two cation-stabilizing alkylthio

(10) For stabilization of β-cation by silyl group, see, for example: (a) Lambert, J. B. *Tetrahedron* **1990**, *46*, 2677. (b) Jarview, A. W. P. *Organomet. Chem. Rev., Sect. A* **1970**, *6*, 153. (c) Colvin, E. W. *Silicon in Organic Synthesis*; Butterworth: London, 1981; Chapter 3.

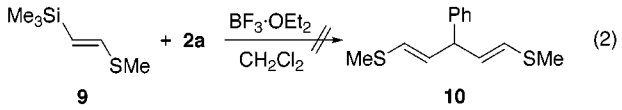
(11) For stabilization of α-cation by thio group, see, for example: Price, C. C.; Oae, S. *Sulfur Bonding*; The Ronald Press Co.: New York, 1962; Chapter 2.

(12) Related allylic cation species, 2-substituted-1,3-dithiolan-2-ylium or 2-substituted-1,3-dithiane-2-ylium salts have been isolated and these salts were reacted with nucleophiles such as silyl enol ethers, stannyl enol ethers and allylstannaes in CH_2Cl_2 to afford corresponding oxoketene dithioacetals and alkenylketene dithioacetals, see: (a) Hashimoto, Y.; Mukaiyama, T. *Chem. Lett.* **1986**, 755. (b) Hashimoto, Y.; Mukaiyama, T. *Chem. Lett.* **1986**, 1623. (c) Hashimoto, Y.; Sugumi, H.; Okauchi, T.; Mukaiyama, T. *Chem. Lett.* **1987**, 1691. (d) Hashimoto, Y.; Sugumi, H.; Okauchi, T.; Mukaiyama, T. *Chem. Lett.* **1987**, 1695.

(13) The allylic alcohol was synthesized in 92% yield by reduction of α-oxoketenedithioacetal with DIBALH (1.5 equiv) in CH_2Cl_2 at −45 °C for 3 h. For the synthesis of α-oxoketenedithioacetal, see: Dieter, R. K. *Tetrahedron* **1986**, *42*, 3029.

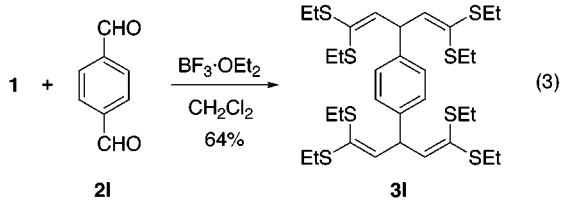
(14) The compound **9** was synthesized in 60% yield from hydroalumination of 2-methylthio-1-trimethylsilylethyne with $LiAlH_4$ in triglyme at 40 °C for 1 day. For an alternative synthesis of **9**, see: Voronkov, M. G.; Rakhlin, V. I.; Mirskov, R. G.; Khangazheev, S. Kh.; Yarosh, O. G.; Tsetlina, E. O. *J. Gen. Chem. USSR* **1979**, 103.

groups[11] at the β-position of vinylsilane are required in this deoxygenative divinylation.



9 **10**

To explore the scope and limitations of this Lewis acid-catalyzed deoxygenative divinylation of aldehydes, the reactions of various aromatic aldehydes **2a**−**l** with **1** under similar conditions were studied. The results are summarized in Table 1. The reaction of *p*-tolualdehyde (**2b**) and 4-methoxybenzaldehyde (**2d**) (benzaldehydes with electron-donating group),or sterically hindered aromatic aldehydes[15] such as *o*-tolualdehyde (**2c**), 1-naphthaldehyde (**2h**), and 2-phenylbenzaldehyde (**2i**) provided the corresponding divinylation products **3b**−**d**,**h**,**i** in lower yields (52−70%) than that of **3a** (entries 10−12, 16, 17). In addition, the reaction of electron-withdrawing group substituted benzaldehydes such as 4-chlorobenzaldehyde (**2e**), 4-nitrobenzaldehyde (**2f**), and 4-cyanobenzaldehyde (**2g**) gave the corresponding divinylation product **3e**−**g** in 78−88% yields (entries 13−15). Not only these simple aromatic aldehydes but also heteroaromatic aldehydes such as 2-furaldehyde (**2j**), 2-thiophenecarboxyaldehyde (**2k**), and terephthalaldehyde (**2l**) readily reacted with **1** to give the corresponding deoxygenative divinylation products **3j**−**l** in moderate to good yields (Scheme 1 and eq 3) (entries 18−20). These results indicated that this deoxygenative divinylation proceeded regardless of the substituent on the benzaldehyde.

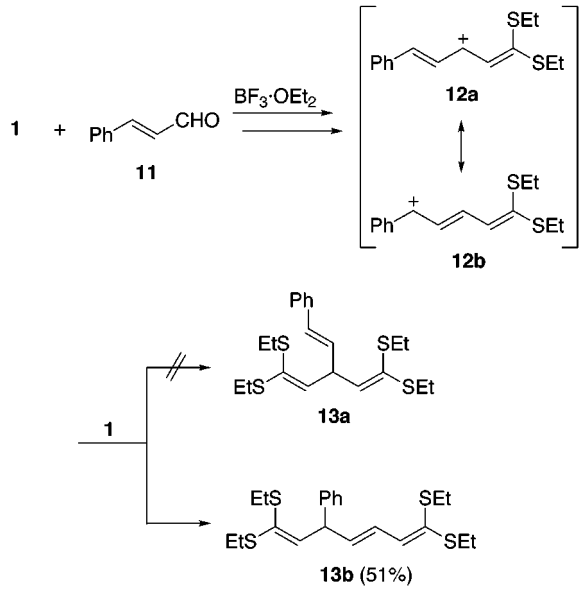


2l **3l**

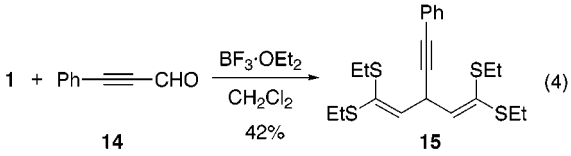
In contrast to aromatic aldehydes, aliphatic aldehydes **2m**−**o** did not react to give the expected divinylation products **3m**−**o** under the above conditions. Instead, the use of $EtAlCl_2$ as Lewis acid produced **3m**−**o** even though their yields are much lower (33−44%) (entries 21−23). The low yields are due to side reactions competing with the formation of the divinylation products.

We furthermore examined the reactivity of **1** toward α,β-unsaturated aldehydes. Cinnamaldehyde (**11**) was treated with **1** (0.5 equiv) in the presence of $BF_3{\cdot}OEt_2$ (0.5 equiv) to afford unexpected deoxygenative 1,3-divinylation product **13b** in moderate yield (51%) (Scheme 3). The formation of **13b** shows that not the allylic cation **12a** but also the conjugated allylic cation **12b** was trapped with **1**. On the contrary, the reaction of related propargyl aldehyde **14** with **1** under similar conditions afforded deoxgenative geminal divinylation product **15** albeit in modest yield (42%) (eq 4). Thus, the Lewis acid-promoted reaction of α,β-unsaturated aldehydes with **1**

Scheme 3



has been found to yield deoxygenative 1,1- or 1,3-divinylation products.



14 **15**

Synthesis of Heterocyclic Compounds via Reaction of *o*-Heteroatom-Functionalized Benzaldehydes with Silylketene Dithioacetal. To extend the synthetic utility of the allylic cation intermediate that is stabilized by the two thio groups, we tried to trap the intermediate with an intramolecular nucleophile such as an NH_2 or OH group. When a mixture of 2-aminobenzaldehyde (**16**) and $BF_3{\cdot}OEt_2$ was treated with **1**, 2-ethylthioquinoline (**19**) was obtained interestingly in 40% yield.[16] The formation of **19** can be reasonably explained by sequence of trapping the allylic cation intermediate **18** with the 2-amino group, deprotonation, and subsequent elimination of ethanethiol (Scheme 4).

On the other hand, treatment of salicylaldehyde (**17**) with **1** under the same conditions produced 4-[2,2-bis(ethylthio)vinyl]-2,2-bis(ethylthio)chroman (**20**) in 58% yield. When **20** was subjected to hydrolysis in the presence of $CuCl_2$−CuO in refluxing acetone containing water, 4-[β,β-bis(ethylthio)vinyl]-3,4-dihydrocoumarin (**21**) was obtained in 85% yield (Scheme 5).

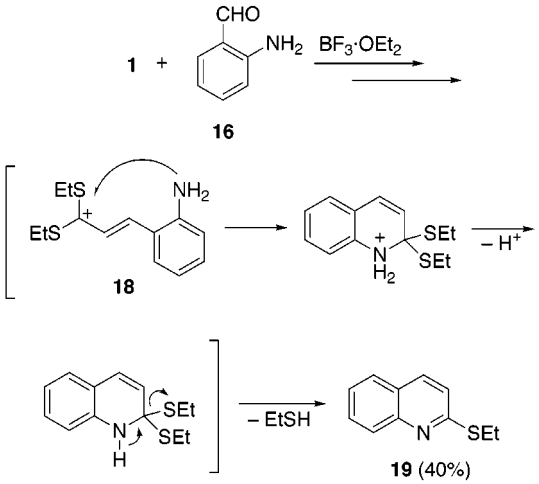
Thus, it is found that the intramolecular cyclization readily takes place to give heterocyclic compounds, when a nucleophilic heteroatom substituent is present at the *o*-position of benzaldehyde.

Reaction of Ketones with Silylketene Dithioacetal. Unlike aldehydes, ketones such as benzophenone, acetophenone, and fluorenone could not be applied to this deoxygenative reaction with **1**, and only unreacted ketones were recovered. To develop applicability of **1** to the reaction with ketones, more reactive α-diketones or α-ketoester was employed. The reaction of benzil (**22a**)

(15) When sterically hindered aromatic aldehydes such as **2c** and **2i** were used, 3-aryl-1,1,3-tris(ethylthio)-1-propene, $ArCH(SEt)CH{=}C(SEt)_2$, were isolated in trace amounts.

(16) For alternative synthesis of 2-ethylthioquinoline, see: Beugelmans, R.; Bois-Choussy, M.; Boudet, B. *Tetrahedron* **1983**, *39*. 4153.

Scheme 4



Scheme 5

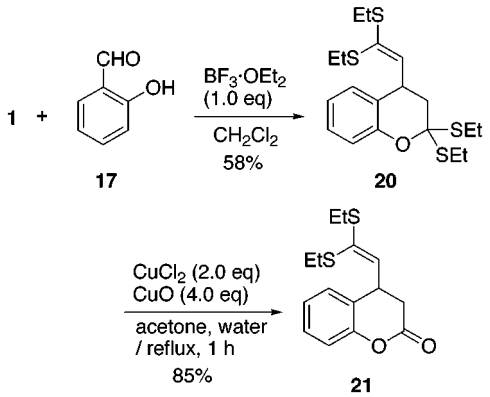


Table 2. Lewis Acid-Promoted Reaction of Silylketene Dithioacetal 1 with α-Diketones 22[a]

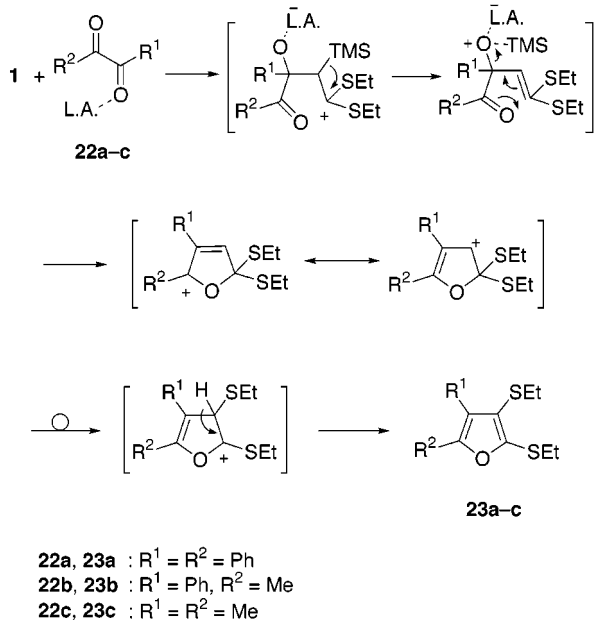
entry	α-diketone **22**	Lewis acid	time, h	product (yield, %)[b]
1	**22a**	BF_3·OEt_2	1.0	**23a** (7)
2	**22a**	$TiCl_4$	1.0	**23a** (34)
3[c]	**22a**	$TiCl_4$	1.0	**23a** (43)[d]
4	**22b**	$TiCl_4$	1.5	**23b** (27)
5	**22c**	$TiCl_4$	2.0	**23c** (23)

[a] All reactions were carried out in CH_2Cl_2 at −78 °C in the presence of 1.0 equiv of Lewis acid. [b] Isolated yield based on silylketene dithioacetal **1**. [c] Excess of **1** (2.2 equiv) was used. [d] Isolated yield based on diketone **22a**.

(1 equiv) with **1** (1 equiv) in the presence of BF_3·OEt_2 (1 equiv) produced unpredicted tetrasubstituted furan **23a** albeit in miserable yield (7%) other than **22a** (90%) (entry 1 in Table 2, Scheme 6). The use of $TiCl_4$, instead of BF_3·OEt_2, fairly improved the yield of **23a** up to 34% (entry 2). Accordingly, similar reaction with 1-phenyl-1,2-propanedione (**22b**) or 2,3-butanedione (**22c**) using $TiCl_4$ was carried out to provide the corresponding tetrasubstituted furan **23b** or **23c** albeit in low yields (23−27% yields) (entries 4, 5). As outlined in Scheme 6, the formation of **23a**−**c** would be reasonably explained by a sequence of deoxygenative addition of **22a**−**c** with **1** to generate the allylic cation, subsequent cyclization to the dihydrofuryl cation accompanying 1,2-migration of an ethylthio group,[17] and elimination of a proton. The low yield of **23a**−**c** would be caused by decomposition of the starting substrate **1**

(17) For example of the 1,2-thio migration, see: Jones, D. K.; Liotta, D. C. *Tetrahedron Lett.* **1993**, *34*, 7209.

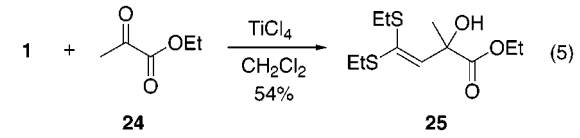
Scheme 6



22a, **23a** : $R^1 = R^2$ = Ph
22b, **23b** : R^1 = Ph, R^2 = Me
22c, **23c** : $R^1 = R^2$ = Me

under acidic conditions of this reaction.[18] This can be reasonably explained by the fact that the use of excess **1** (2.2 equiv) as a proton scavenger produced **23a** in higher yield (43%) (entry 3 in Table 2).

We further attempted to apply this Lewis acid-promoted reaction to an α-ketoester. Treatment of $TiCl_4$-activated ethyl pyruvate (**24**) with **1** produced only allylic alcohol **25** in 54% yield, but no furan derivative was obtained (eq 5).



Conclusion. We note the following results from this investigation: (1) silylketene dithioacetal **1** was reacted with aromatic, aliphatic and α,β-unsaturated aldehydes in the presence of a catalytic or an equimolar amount of Lewis acid to produce deoxygenative 1,1- or 1,3-divinylation products. (2) A new synthetic approach to functionalized quinoline and chroman was developed by the Lewis-acid-promoted reaction of *o*-heteroatom-substituted benzaldehydes with **1**. (3) The $TiCl_4$-promoted reaction of α-diketones or an α-ketoester with **1** led to tetrasubstituted furans or an allylic alcohol.

Experimental Section

Materials. Dichloromethane was distilled from P_2O_5. THF and diethyl ether were distilled from sodium benzophenone ketyl in a recycling still. Diisopropylamine (DIA), BF_3·OEt_2, and $TiCl_4$ were distilled from CaH_2. Commercial solutions of BuLi (1.54 M in hexane) and $EtAlCl_2$ (0.93 M in hexane) were used. Me_3SiCH_2Cl was purchased from Shin-Etsu Chemical.

General Methods. ^1H and ^{13}C NMR spectra were obtained in $CDCl_3$, operating ^1H NMR at 400 or 500 MHz and ^{13}C NMR at 101 or 126 MHz with Me_4Si as an internal standard. IR

(18) Silylketene dithioacetal **1** undergoes hydrolysis on treatment with silica gel. For other examples of decomposition of silylketene dithioacetal by acid, see: ref 6 and 7a.

spectra were recorded of thin firm on KBr plates. Mass spectra were recorded at 70 eV. Melting points were measured in open capillary tubes and are uncorrected.

General Procedure for the Synthesis of 1,1,5,5-Tetrakis(ethylthio)-1,4-pentadienes (3a−o, 15), (*E*)-1,1,7,7-Tetrakis(ethylthio)-5-phenyl-1,3,6-heptatriene (13b), and 4-[2,2-Bis(ethylthio)vinyl]-2,2-bis(ethylthio)chroman (20). To a solution of aldehyde **2a**−**o**, **11**, **14**, or **17** (0.23 or 0.45 mmol) in CH_2Cl_2 (3 mL) was added BF_3·OEt_2 (32.6 mg, 0.23 mmol) or $EtAlCl_2$ (0.47 mL, 0.46 mmol) at −78 °C. Then a solution of **1** (100 mg, 0.45 mmol) in CH_2Cl_2 (3 mL) was added dropwise to the mixture. The reaction mixture was stirred for 1−2 h at this temperature. The reaction was quenched by addition of phosphate buffer (pH = 7), and the organic layer was extracted with CH_2Cl_2, washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was chromatographed on preparative TLC (silica gel, AcOEt/hexane = 1:10) to afford **3a**−**o**, **13b**, **15**, and **20**. The reaction conditions and yields of **3a**−**o** are summarized in Table 1. The compounds **3a**,**j**,**l**,**m**, **13b**, and **20** had the following properties. The properties for compounds **3b**−**i**,**k**,**n**,**o** and **15** are provided in the Supporting Information.

1,1,5,5-Tetrakis(ethylthio)-3-phenyl-1,4-pentadiene (3a): colorless oil; IR (neat) 1600, 1492, 1448, 1259, 755, 698 cm^{-1}; ^1H NMR (500 MHz) δ 1.22 (6H, t, J = 7.3 Hz), 1.22 (6H, t, J = 7.3 Hz), 2.68−2.83 (8H, m), 5.63 (1H, t, J = 9.5 Hz), 6.21 (2H, d, J = 9.5 Hz), 7.17−7.30 (5H, m); ^{13}C NMR (126 MHz) δ 14.3, 15.2, 27.0, 27.2, 47.5, 126.3, 127.4, 128.6, 131.1, 138.7, 142.8. Anal. Calcd for $C_{19}H_{28}S_4$: C, 59.32; H, 7.34. Found: C, 59.14; H, 7.27.

1,1,5,5-Tetrakis(ethylthio)-3-(2-furyl)-1,4-pentadiene (3j): yellow oil; IR (neat) 1502, 1448, 1259, 1008, 730 cm^{-1}; ^1H NMR (500 MHz) δ 1.23 (12H, t, J = 7.3 Hz), 2.68−2.83 (8H, m), 5.66 (1H, t, J = 9.2 Hz), 5.99−5.99 (1H, m), 6.12 (2H, d, J = 9.2 Hz), 6.27−6.27 (1H, m), 7.32−7.32 (1H, m); ^{13}C NMR (126 MHz) δ 14.1, 15.1, 26.9, 27.3, 42.4, 105.0, 110.1, 132.1, 134.0, 141.6, 154.9. Anal. Calcd for $C_{17}H_{26}OS_4$: C, 54.50; H, 6.99. Found: C, 54.69; H, 7.01.

1,4-Bis[1,1,5,5-tetrakis(ethylthio)-1,4-pentadiene-3-yl]-benzene (3l): yellow oil; IR (neat) 1504, 1446, 1373, 1201, 831, 755 cm^{-1}; ^1H NMR (500 MHz) δ 1.21 (12H, t, J = 7.3 Hz), 1.22 (12H, t, J = 7.3 Hz) 2.67−2.84 (16H, m), 5.59 (2H, t, J = 9.5 Hz), 6.16 (4H, d, J = 9.5 Hz), 7.12 (4H, s); ^{13}C NMR (126 MHz) δ 14.2, 15.1, 26.9, 27.2, 47.1, 127.5, 130.9, 138.6, 140.6. Anal. Calcd for $C_{32}H_{50}S_8$: C, 55.60; H, 7.29. Found: C, 55.98; H, 7.34.

1,1,5,5-Tetrakis(ethylthio)-3-(2-phenylethyl)-1,4-pentadiene (3m): yellow oil; IR (neat) 1496, 1452, 1373, 1259, 750, 698 cm^{-1}; ^1H NMR (500 MHz) δ 1.22 (6H, t, J = 7.3 Hz), 1.22 (6H, t, J = 7.3 Hz), 1.71 (2H, tt, J = 8.3, 7.6 Hz), 2.60 (2H, t, J = 8.3 Hz), 2.61−2.81 (8H, m) 4.34 (1H, dt, J = 9.3 Hz, 7.6 Hz), 5.98 (2H, d, J = 9.3 Hz), 7.15−7.28 (5H, m); ^{13}C NMR (126 MHz) δ 14.2, 15.1, 26.8, 27.1, 33.6, 37.8, 43.1, 125.7, 128.3, 128.3, 130.0, 140.8, 142.3. Anal. Calcd for $C_{21}H_{32}S_4$: C, 61.11; H, 7.81. Found: C, 60.83; H, 7.81.

(*E*)-1,1,7,7-Tetrakis(ethylthio)-5-phenyl-1,3,6-heptatriene (13b): yellow oil; IR (neat) 1492, 1446, 1259, 970, 757, 698 cm^{-1}; ^1H NMR (500 MHz) δ 1.21 (3H, t, J = 7.3 Hz), 1.22 (3H, t, J = 7.3 Hz), 1.24 (3H, t, J = 7.3 Hz), 1.25 (3H, t, J = 7.3 Hz), 2.71−2.82 (8H, m), 4.99 (1H, dd, J = 7.2, 7.2 Hz), 5.89 (1H, dd, J = 15.3, 6.7 Hz), 6.25 (1H, d, J = 9.5 Hz), 6.61 (1H, d, J = 10.4 Hz), 6.78 (1H, ddd, J = 15.3 Hz, 10.4 Hz, 1.2 Hz), 7.2−7.3 (5H, m); ^{13}C NMR (126 MHz) δ 14.3, 14.4, 15.0, 15.3, 26.9, 27.1, 27.1, 27.8, 49.4, 126.5, 127.7, 127.9, 128.6, 130.6, 131.3, 133.8, 135.9, 139.5, 142.8. Anal. Calcd for $C_{21}H_{30}S_4$: C, 61.41; H, 7.36. Found: C, 61.10; H, 7.39.

4-[2,2-Bis(ethylthio)vinyl]-2,2-bis(ethylthio)chroman (20): white crystal; mp 76.0−77.0 °C; IR (KBr) 1581, 1484, 1448, 1220, 1004, 916, 757 cm^{-1}; ^1H NMR (500 MHz) δ 1.23 (3H, t, J = 7.3 Hz), 1.28 (3H, t, J = 7.3 Hz), 1.28 (3H, t, J = 7.16 Hz), 1.30 (3H, t, J = 7.16 Hz), 2.30 (1H, dd, J = 13.9, 11.2 Hz), 2.39 (1H, dd, J = 13.9, 6.1 Hz), 2.75−2.93 (8H, m), 4.73 (1H, ddd, J = 11.2, 9.2, 6.1 Hz), 6.02 (1H, d, J = 9.2 Hz), 6.85−7.16 (4H, m); ^{13}C NMR (126 MHz) δ 14.2, 14.5, 14.6, 15.2, 24.2, 24.5, 26.9, 27.1, 35.6, 39.6, 94.0, 117.3, 121.7, 123.7, 127.9, 128.5, 133.0, 138.8, 152.2. Anal. Calcd for $C_{19}H_{28}OS_4$: C, 56.95; H, 7.04. Found: C, 56.84; H, 7.05.

Synthesis of 2-Ethylthioquinoline (19). To a solution of 2-aminobenzaldehyde **16**[20] (27.5 mg, 0.23 mmol) and **1** (50.0 mg, 0.23 mmol) in CH_2Cl_2 (3 mL) was added BF_3·OEt_2 (32.2 mg, 0.23 mmol) at −78 °C. The reaction mixture was stirred for 1.5 h at this temperature. After similar workup, the residue was chromatographed on preparative TLC (silica gel, AcOEt/hexane = 1:10) to afford **19** (17.0 mg, 0.09 mmol, 40%) as a yellow oil: IR (neat) 1614, 1592, 1556, 1496, 1419, 1294, 1137, 1089, 815, 748 cm^{-1}; ^1H NMR (500 MHz) δ 1.45 (3H, t, J = 7.5 Hz), 3.35 (2H, q, J = 7.5 Hz), 7.20 (1H, d, J = 8.5 Hz), 7.41 (1H, ddd, J = 8.5, 7.6, 1.3 Hz), 7.64 (1H, ddd, J = 8.5, 7.6, 1.3 Hz), 7.70 (1H, dd, J = 8.5, 1.3 Hz), 7.87 (1H, d, J = 8.5 Hz), 7.93 (1H, d, J = 8.5 Hz); ^{13}C NMR (126 MHz) δ 14.6, 24.2, 121.0, 125.1, 125.9, 127.6, 128.0, 129.5, 135.2, 148.4, 159.5. The spectral data of **19** were consistent with those of the compound **19**[16] reported previously.

Hydrolysis of 20. Hydrolysis of **20** was carried out by using **20** (50 mg, 0.125 mmol), $CuCl_2$ (53.6 mg, 0.25 mmol), and CuO (39.8 mg, 0.5 mmol) in acetone−H_2O, according to the established procedure.[21] After similar workup, the residue was chromatographed on preparative TLC (silica gel, AcOEt/hexane = 1:10) to afford **21** (29.5 mg, 0.1 mmol, 80%) as a yellow oil: IR (neat) 1774, 1484, 1454, 1216, 1147, 919, 757 cm^{-1}; ^1H NMR (400 MHz) δ 1.26 (6H, t, J = 7.3 Hz), 2.64 (1H, dd, J = 15.8, 9.6 Hz), 2.74−2.89 (5H, m), 4.63 (1H, ddd, J = 12.3, 9.2, 5.6 Hz), 5.97 (1H, d, J = 9.2 Hz), 7.06−7.16 (3H, m), 7.26−7.29 (1H, m); ^{13}C NMR (101 MHz) δ 14.0, 15.1, 26.9, 27.2, 35.0, 35.9, 117.1, 124.6, 125.0, 127.1, 128.6, 134.3, 134.9, 151.4, 167.5. Anal. Calcd for $C_{15}H_{18}O_2S_4$: C, 61.19; H, 6.16. Found: C, 61.21; H, 6.16.

Reaction of Ketones 22a−c or Ethyl Pyruvate (24) with 1. General Procedure. To a solution of diketone (**22a**−**c**) or ethyl pyruvate (**24**) (0.36 mmol) in CH_2Cl_2 (2 mL) was added $TiCl_4$ (63.8 mg, 0.36 mmol) at −78 °C. Then **1** (80 mg, 0.363 mmol) in CH_2Cl_2 (2 mL) was added dropwise to the mixture. The mixture was stirred for 1−2 h at this temperature. After similar workup, the residue was chromatographed on preparative TLC (silica gel, AcOEt/hexane = 1:10) to afford **23a**−**c** or **25**. The reaction conditions and yields of **23a**−**c** and **25** are summarized in Table 2 and eq 5. The compounds **23a**, **b** and **25** have the following properties. The property for compound **23c** is provided in the Supporting Information.

2,3-Bis(ethylthio)-4,5-diphenylfuran (23a): white crystal; mp 54−55.5 °C; IR (KBr) 1492, 1444, 1259, 948, 767, 698 cm^{-1}; ^1H NMR (500 MHz) δ 1.04 (3H, t, J = 7.3 Hz), 1.39 (3H, t, J = 7.32 Hz), 2.40 (2H, q, J = 7.32 Hz), 3.00 (2H, q, J = 7.32 Hz), 7.18−7.44 (10H, m); ^{13}C NMR (126 MHz) δ 14.6, 15.4, 28.9, 29.6, 122.6, 125.6, 126.0, 127.6, 127.7, 128.3, 128.6, 130.1, 130.3, 132.8, 149.0, 150.9. Anal. Calcd for $C_{20}H_{20}OS_2$: C, 70.55; H, 5.92. Found: C, 70.37; H, 5.97.

2,3-Bis(ethylthio)-5-methyl-4-phenylfuran (23b): yellow oil; IR (neat) 1498, 1444, 1259, 1008, 748, 700 cm^{-1}; ^1H NMR (500 MHz) δ 1.01 (3H, t, J = 7.3 Hz), 1.32 (3H, t, J = 7.3 Hz), 2.33 (3H, s), 2.39 (2H, q, J = 7.32 Hz), 2.89 (2H, q, J = 7.32 Hz), 7.30−7.44 (5H, m); ^{13}C NMR (126 MHz) δ 14.9, 14.5, 15.2, 28.8, 30.0, 121.9, 125.0, 127.1, 128.2, 129.4, 132.5, 146.9, 151.3. Anal. Calcd for $C_{15}H_{18}OS_2$: C, 64.70; H, 6.52. Found: C, 64.52; H, 6.50.

Ethyl 4,4-bis(ethylthio)-2-hydroxy-2-methyl-3-butenate (25): yellow oil; IR (neat) 3496, 1731, 1571, 1448, 1373, 1243, 1124 cm^{-1}; ^1H NMR (400 MHz) δ 1.23 (3H, t, J = 7.3 Hz), 1.25 (3H, t, J = 7.3 Hz), 1.28 (3H, t, J = 7.2 Hz), 1.56 (3H, s), 2.70−2.85 (4H, m), 4.17−4.27 (2H, m), 4.45 (1H, s),

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6.23 (1H, s); ^{13}C NMR (101 MHz) δ 13.9, 14.0, 14.8, 27.0, 27.3, 27.6, 61.8, 73.7, 134.5, 138.4, 174.9. Anal. Calcd for $C_{11}H_{20}O_3S_2$: C, 49.97; H, 7.62. Found: C, 49.77; H, 7.54.

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Supporting Information Available: Experimental procedures and spectral and analytical data for compounds **1**, **3b**–**i**,**k**,**n**,**o**, **8**, **9**, **15**, and **23c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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