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Synthesis of Functionalized Allylic Sulfoxides and Their Use in the Construction of 2,3,4-Trisubstituted Furans via a [3 + 2] Annulation

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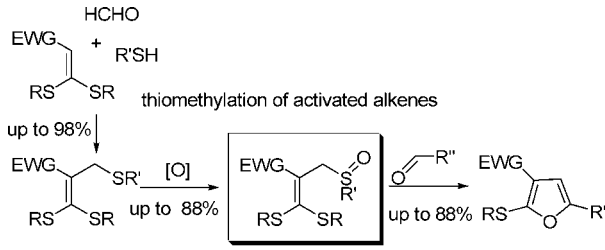

[3 + 2] annulation strategy toward furan synthesis

A route to 2,3,4-trisubstituted furan derivatives based on a [3 + 2] annulation of functionalized allylic sulfoxides and aldehydes is described. In this strategy, the precursors of allylic sulfoxides **4**, allylic sulfides **3**, were synthesized via a thiomethylation reaction of an α-EWG ketene-*S*,*S*-acetal **1** (EWG: electron-withdrawing group), formaldehyde, and a thiol **2** in high to excellent yields. Allylic sulfoxides **4** were prepared by a highly regioselective oxidation of **3**, using *m*-chloroperoxybenzoic acid as oxidant. Thus, starting from these readily available sulfoxides **4**, 2-alkylthio-3,4-disubstituted furans **6** were efficiently constructed via the [3 + 2] annulation reaction of **4** with aldehydes **5** under mild conditions. Further replacement of the 2-alkylthio group of **6** with amines led to the formation of 2-amino-3,4-disubstituted furan derivatives **7**.

Introduction

Functionalized ketene-*S*,*S*-acetals are versatile intermediates in organic synthesis (Figure 1).[1−4] Among them, α-EWG ketene-*S*,*S*-acetals (EWG: electron-withdrawing group) have proven to be especially important in the construction of a diverse

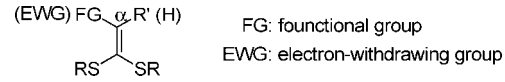

FIGURE 1. Structure of functionalized ketene-*S*,*S*-acetals.

array of polysubstituted carbo-[1,5] and heterocyclic compounds.[1,6,7] Some recent research has revealed that the highly polarized push (RS)−pull (EWG) interaction on the C−C double bond of α-EWG ketene-*S*,*S*-acetals makes their α-carbon atom a potential nucleophilic center and the coupling reaction at the nucleophilic α-carbon atom of these *β*,*β*-dialkylthio activated alkenes is reliable and incorporates a wide variety of carbon[8,9] and heteroatom electrophiles.[10] As a continuation of our interest in the design and discovery of potentially synthetically useful intermediates based on ketene-*S*,*S*-acetals,[5,6,8,10] in the present research, a thiomethylation of α-EWG ketene-*S*,*S*-acetals **1** with formaldehyde and thiols **2**, the first example of the thiomethylation of activated alkenes as nucleophiles, was achieved to furnish a set of allylic sulfides **3** bearing the structural feature of ketene-*S*,*S*-acetals (Scheme 1). Thus, a route toward 2-alkylthio/2-amino-3,4-disubstituted furans **6/7** has been established based on a [3 + 2] annulation strategy of allylic sulfoxides **4** (the oxidated products of **3**) and aldehydes **5** (Scheme 1). In

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(3) For synthesis and synthetic applications of fluorinated ketene-*S*,*S*-acetals, see: (a) Muzard, M.; Portella, C. *J. Org. Chem.* **1993**, *58*, 29–31. (b) Pirrung, M. C.; Rowley, E. G.; Holmes, C. P. *J. Org. Chem.* **1993**, *58*, 5683–5689. (c) Sotoca, E.; Bouillon, J.-P.; Gil, S.; Parra, M.; Portella, C. *Tetrahedron* **2005**, *61*, 4395–4402, and references cited therein.

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(5) For selected examples, see: (a) Bi, X.; Dong, D.; Liu, Q.; Pan, W.; Zhao, L.; Li, B. *J. Am. Chem. Soc.* **2005**, *127*, 4578–4579. (b) Zhang, Q.; Sun, S.; Hu, J.; Liu, Q.; Tan, J. *J. Org. Chem.* **2007**, *72*, 139–143. (c) Gill, S.; Kocienski, P.; Kohler, A.; Pontiroli, A.; Liu, Q. *Chem. Commun.* **1996**, 1743–1744.

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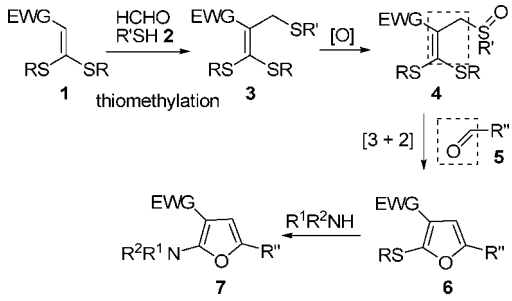
SCHEME 1



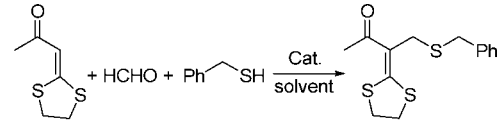
this paper, two reactions, the [3 + 2] annulation reaction of **4** and **5** to polysubstituted furans **6** and the thiomethylation reaction of **1** to functionalized allylic sulfides **3**, are described in detail.

Results and Discussion

Preparation of Starting Materials. According to the procedure reported previously,[11] α-EWG ketene-*S*,*S*-acetals **1a**−**h** were conveniently prepared by a two-step process involving the preparation of α-EWG α-acetyl ketene-*S*,*S*-acetals starting from the corresponding *β*-dicarbonyl compounds, carbon disulfide, and alkyl halides in the presence of K_2CO_3 catalyzed by tetrabutylammonium bromide (TBAB) in water and the sequential acid-promoted deacylation, respectively.

Synthesis of α-EWG-α′-alkyl/arylthiomethyl Ketene-*S*,*S*-acetals 3 via Thiomethylation of α-EWG Ketene-*S*,*S*-acetals 1. For the preparation of synthetically useful allylic sulfides,[12,13] although some elegant methods, such as transition metal catalyzed alkylation of thiols,[14a−c] allylation of diorganodisulfides with allyl halides,[14d] or indium-promoted one-pot reaction of Baylis−Hillman acetates, sodium thiosulfate, and allyl bromide,[14e] etc., have been developed, to our knowledge, none of them[12−14] involved a Mannich-type thiomethylation[15] of activated alkenes, a simple method leading directly to allylic sulfides with water as the only byproduct. In fact, in the three-component thiomethylation reaction involving a nucleophile, formaldehyde, and a thiol, various carbon nucleophiles (such as ketones, nitroalkanes, phenols, aromatic amines, electron-rich heterocyclic compounds, or even ferrocene) and heteroatom nucleophiles (including nitrogen, oxygen, sulfur, phosphorus, or halogens) have been proven to be effective.[15] However, the investigation of taking activated alkenes as carbon nucleophiles in thiomethylation has been scarce. Kirk[16a] and Cohen[16b] reported that the formal thiomethylated products of activated alkenes could be achieved, for example, by refluxing a mixture of cyclopent-2-enone, formaldehyde, and thiophenol in the presence of triethylamine for 4 days to afford 2-(phenylthiomethyl)cyclopent-2-enone in 73% yield. But the reaction was proved to proceed in a non-Mannich-type process in which the corresponding thia-Michael adduct, 3-(phenylthio)cyclopentanone, was obtained as the intermediate.[16b]

TABLE 1. Optimization of Conditions for Thiomethylation of 1a with Formaldehyde and Benzylthiol 2a[a]



1a 2a 3a

entry	catalyst	solvent	**1a**:HCHO:**2a**	yield of **3a** (%)[b]
1	HCl	THF	1:1:1	36
2	HCl	THF	1:2:1	97
3	HCl	EtOH	1:2:1	52
4		AcOH	1:2:1	83
5		THF	1:2:1	—[c]

[a] **1a** (1.0 mmol), HCHO (40% aqueous), **2a** (1.0 mmol), HCl (2.0 mmol, 36% aqueous), solvent (2.0 mL), rt, 0.5 h. [b] Isolated yields. [c] 24 h, no reaction.

As part of our research to assess α-EWG ketene-*S*,*S*-acetals **1** as activated alkenes in the C−C bond forming reactions with carbon electrophiles,[8] we showed that the α-carbon atom of **1** has high nucleophilicity. Encouraged by these results and the foreseeable possibility of the thiomethylation based on α-EWG ketene-*S*,*S*-acetals, we decided to investigate the thiomethylation reaction of these activated alkenes with formaldehyde and thiols under acidic conditions. Thus, hydrochloric acid (2.0 mmol, 36% aqueous) was initially evaluated in the model reaction of 1-(1,3-dithiolan-2-ylidene)propan-2-one **1a** (1.0 mmol) with benzylthiol **2a** (1.0 mmol) and formaldehyde (1.0 mmol, 40% aqueous) in THF (2.0 mL). As depicted in Table 1, the reaction could furnish the thiomethylated product, 4-(benzylthio)-3-(1,3-dithiolan-2-ylidene)butan-2-one **3a**, as a white solid in 36% isolated yield after reacting for 0.5 h (Table 1, entry 1). Notably, a 2-fold excess of formaldehyde could dramatically increase the yield of **3a** to 97% under identical conditions (entry 2). Comparatively, ethanol was an unfavorable solvent for this process (entry

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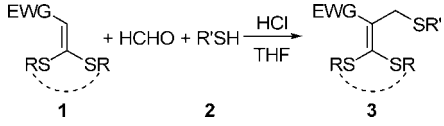
TABLE 2. Acid-Catalyzed Thiomethylation of 1 with Formaldehyde and Thiols 2[a]



1 2 3

entry	1	EWG	R or R, R	2	R′	3	time (h)	yield of 3 (%)[b]
1	**1a**	MeCO	$(CH_2)_2$	**2a**	Bn	**3a**	0.5	97
2	**1b**	MeCO	$(CH_2)_3$	**2a**	Bn	**3b**	0.5	72
3	**1c**	MeCO	Me	**2a**	Bn	**3c**	0.5	93
4	**1d**	MeCO	Et	**2a**	Bn	**3d**	0.5	97
5	**1e**	MeCO	Bn	**2a**	Bn	**3e**	0.5	78
6	**1f**	PhCO	Me	**2a**	Bn	**3f**	4.0	92
7	**1g**	PhCO	Et	**2a**	Bn	**3g**	4.0	98
8	**1h**	CO_2Et	Me	**2a**	Bn	**3h**	6.0	83
9	**1d**	MeCO	Et	**2b**	Et	**3i**	0.5	98
10	**1d**	MeCO	Et	**2c**	n-$C_{12}H_{25}$	**3j**	0.5	71
11	**1d**	MeCO	Et	**2d**	Ph	**3k**	8.0	72
12	**1d**	MeCO	Et	**2e**	4-MeC_6H_4	**3*l***	8.0	83
13	**1d**	MeCO	Et	**2f**	4-ClC_6H_4	**3m**	8.0	97

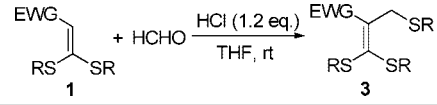
[a] **1** (1.0 mmol), HCHO (2.0 mmol, 40% aqueous), **2** (1.0 mmol), HCl (2.0 mmol, 36% aqueous), THF (2.0 mL), rt. [b] Isolated yields.

3). In the case of the reaction performed in neat acetic acid (without HCl, entry 4) for 0.5 h, **3a** was also obtained in 83% yield. But no reaction was detected when the reaction was carried out without HCl in THF (entry 5).

Under the optimized conditions (Table 1, entry 2), a range of reactions were carried out with selected substrates **1** and thiols **2**. As described in Table 2, all of the reactions between formaldehyde, thiols **2** (including substituted thiophenols) and α-EWG ketene-*S*,*S*-acetals **1** proceeded smoothly in acidic aqueous media to afford α-EWG-α′-alkyl/arylthiomethyl ketene-*S*,*S*-acetals **3a**−**m** in one pot, and the yield reached up to 98%. Clearly, the above results show the wide scope of the thiomethylation reaction with respect to a range of α-EWG ketene-*S*,*S*-acetals **1** and thiols **2**. We therefore present here a facile and efficient protocol for the synthesis of functionalized allylic sulfides **3** based on ketene-*S*,*S*-acetals.

In the next study, the thiomethylations of α-EWG ketene-*S*,*S*-acetals **1**, in which compounds **1** were not only used as an activated alkenes but also served as thiol sources, were performed to extend the synthetic application of **1** as the odorless thiol equivalents.[17] As expected, the thiomethylation of **1c** readily occurred to afford the desired allylic sulfide **3n** in 85% yield (Table 3, entry 1) when **1c** (1.0 mmol) was treated with formaldehyde in the presence of 1.2 equiv of HCl (36% aqueous) in THF. Similarly, the selected acyclic ketene-*S*,*S*-acetals **1d**, **1e**, **1f**, **1g**, and **1h** could also give the corresponding **3i**, **3e**, **3o**, **3p**, and **3q** in good to excellent yields (entries 2−6) under identical reaction conditions. Notably, this simple and efficient alternative procedure can avoid the use of foul-smelling thiols, especially the volatile methanethiol and ethanethiol.

TABLE 3. Acid-Catalyzed Thiomethylation of 1 with Formaldehyde[a]

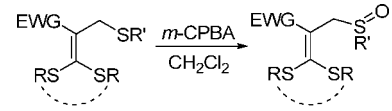


1 3

entry	1	EWG	R	3	time (h)	yield (%)[b]
1	**1c**	MeCO	Me	**3n**	2.0	85
2	**1d**	MeCO	Et	**3i**	4.5	97
3	**1e**	MeCO	Bn	**3e**	12.0	66
4	**1f**	PhCO	Me	**3o**	12.0	86
5	**1g**	PhCO	Et	**3p**	13.0	85
6	**1h**	CO_2Et	Me	**3q**	12.0	91

[a] **1** (1.0 mmol), HCHO (2.0 mmol, 40% aqueous), HCl (1.2 mmol, 36% aqueous), THF (2.0 mL), rt. [b] Isolated yields.

TABLE 4. Regioselective Oxidation of Allylic Sulfides 3[a]



3 4

entry	3	EWG	R	R′	4	yield (%)[b]
1	**3a**	MeCO	$(CH_2)_2$	Bn	**4a**	84
2	**3d**	MeCO	Bn	Bn	**4d**	86
3	**3k**	MeCO	Et	Ph	**4k**	72
4	**3l**	MeCO	Et	4-MeC_6H_4	**4l**	79
5	**3n**	MeCO	Me	Me	**4n**	84
6	**3o**	PhCO	Me	Me	**4o**	88
7	**3p**	PhCO	Et	Et	**4p**	86
8	**3q**	CO_2Et	Me	Me	**4q**	85

[a] **3** (1.0 mmol), *m*-CPBA (1.0 mmol), CH_2Cl_2 (5.0 mL), 0 °C, 0.5 h. [b] Isolated yields.

Regioselective Oxidation of Allylic Sulfides 3 with *m*-CPBA to Afford Allylic Sulfoxides 4. In some cases, oxidations of allylic sulfides with electrophilic oxidants have problems in selectivity.[12,18] In contrast, the oxidation of α-EWG-α′-alkyl/arylthiomethyl ketene-*S*,*S*-acetals **3** with *m*-chloroperoxybenzoic acid (*m*-CPBA) as oxidant has perfect regioselectivity in our experiments. As described in Table 4, treatment of selected **3** (1.0 mmol) with *m*-CPBA (1.0 mmol) in dichloromethane (5.0 mL) at 0 °C for 0.5 h can furnish α-EWG-α′-alkyl/arylsulfinylmethyl ketene-*S*,*S*-acetals **4** in 72−88% isolated yields, respectively. It is clear that the oxidations of **3**, including aryl sulfides **3k** and **3*l*** (entries 3 and 4), occur selectively at the allylic sulfide moiety with the dithioacetal residue intact.

Synthesis of Furans 6 by a Novel [3 + 2] Annulation of Allylic Sulfoxides 4 with Aldehydes 5. Furans are important five-membered heterocycles which are frequently occurring structural subunits in numerous natural products with interesting biological activities,[19] and are also versatile building blocks in organic synthesis.[20] Most known methods for the construction of furan scaffold proceed via various types of cyclization or

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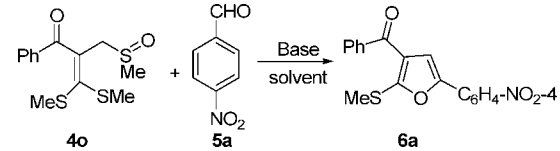
cycloisomerization of acyclic precursors,[21] for example, the cyclocondensation of 1,4-dicarbonyl compounds or equivalents (Paal−Knorr synthesis),[22] the condensation of simple β-dicarbonyl compounds with α-haloketones (Feist−Benary synthesis),[23] and the cycloisomerization of alkyne- and allene-containing compounds.[21b,24] Recently, some new strategies for furan synthesis, such as the annulation of ketimines with aldehydes,[25a] fluoropropargyl chloride with carbonyl compounds,[25b] α,β-acetylenic ketones with α-diazo esters,[25c] ynolates with α-acyloxyketones,[25d] and 2,3-bis(trimethylsilyl)buta-1,3-diene with acyl chlorides,[25e] have been well developed.

In the present research, the reactions of the functionalized allylic sulfides/sulfoxides **3**/**4** with aldehydes were attempted under the consideration that a [3 + 2] annulation strategy[26] would be realized for the construction of substituted furans (Scheme 1). However, several initial efforts were unsuccessful in the reactions of allylic sulfide **3o** and 4-nitrobenzaldehyde **5a** in the presence of either NaOH in EtOH, or *t*-BuOK in THF, or NaH in THF, or NaH in DMSO.

Then, we turned to the more reactive allylic sulfoxides **4** as the three carbon components and the reaction of **4o** with **5a** using 2.0 equiv of NaOH as base in EtOH was carried out. To our delight, 2-methylthio-3-benzoyl-5-(4-nitrophenyl)furan **6a** was obtained in 76% isolated yield by reacting for 4.0 h at room temperature (Table 5, entry 1). Thus, compound **4o** was used as model substrate to optimize the reaction conditions. As described in Table 5, various bases, such as NaOH/MeOH, *t*-BuOK/THF, and NaH/DMSO, were selected for this annulation. It was observed that the annulated product **6a** could be obtained in all cases (entries 2−4). Among them, NaOH/EtOH was proved to be more effective regarding the yields and reaction times. In addition, the amount of NaOH and solvent were also examined. By comparison (entries 5−7), the best results were obtained when **4o** (1.0 mmol) was treated with **5a** (1.1 mmol) in EtOH (2.0 mL) in the presence of NaOH (4.0 mmol) at room temperature for 1.5 h, thus providing **6a** in 88% isolated yield (entry 5).

For a more general understanding of the scope of this [3 + 2] annulation strategy, a variety of aldehydes **5** were selected to react with **4o** under the optimized conditions and the experimental results are given in Table 6. It was found that all arylaldehydes tested, including benzaldehyde (entry 7), arylaldehydes with both electron-withdrawing (entries 1−6) and electron-donating groups (entries 8 and 9), and heteroaromatic aldehydes (entries 10 and 11), could readily react with **4o** to afford 2-alkylthio-3,4-disubstituted furans **6a**−**k** in good to high yields. For comparison, the reactions of electron-rich arylaldehydes give slightly lower yields (entries 8−11). However, the reactions of aliphatic aldehydes (acetaldehyde, cyclohexanecarbaldehyde, or pivalaldehyde) with **4o** led to a complex mixture in which no type **6** could be detected. The tolerance of substrate **4** was then investigated. It was found that the variation of the

TABLE 5. Optimization of Conditions for [3 + 2] Annulation Reaction of 4o with 5a[a]

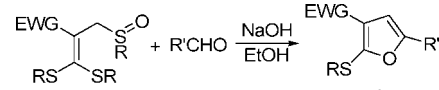


4o **5a** **6a**

entry	base (equiv)	solvent (V/mL)	time (h)	yield (%)[b]
1	NaOH (2.0)	EtOH (2.0)	4.0	76
2	NaOH (2.0)	MeOH (2.0)	14.0	43
3	*t*-BuOK (2.0)	THF (2.0)	14.0	74
4	NaH (2.0)	DMSO (2.0)	1.0	64
5	NaOH (4.0)	EtOH (2.0)	1.5	88
6	NaOH (4.0)	EtOH (5.0)	5.0	82
7	NaOH (4.0)	EtOH (10.0)	7.0	73

[a] **4o** (1.0 mmol), **5a** (1.1 mmol), rt, then quenched by dilute HCl at 0 °C. [b] Isolated yields.

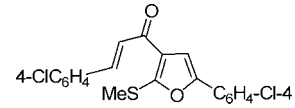
TABLE 6. [3 + 2] Annulation Reaction of 4 with 5[a]



4 **5** **6**

entry	4	EWG	R	5	R′	time (h)	6	yield (%)[b]
1	**4o**	PhCO	Me	**5a**	4-$NO_2C_6H_4$	1.5	**6a**	88
2	**4o**	PhCO	Me	**5b**	3-$NO_2C_6H_4$	1.5	**6b**	73
3	**4o**	PhCO	Me	**5c**	2-ClC_6H_4	2.0	**6c**	60
4	**4o**	PhCO	Me	**5d**	4-ClC_6H_4	2.0	**6d**	61
5	**4o**	PhCO	Me	**5e**	4-FC_6H_4	2.0	**6e**	61
6	**4o**	PhCO	Me	**5f**	4-pyridinyl	1.5	**6f**	85
7	**4o**	PhCO	Me	**5g**	Ph	3.0	**6g**	59
8	**4o**	PhCO	Me	**5h**	4-$CH_3C_6H_4$	5.0	**6h**	55
9	**4o**	PhCO	Me	**5i**	3,4-$O_2CH_2C_6H_3$	4.0	**6i**	54
10	**4o**	PhCO	Me	**5j**	2-furyl	2.0	**6j**	61
11	**4o**	PhCO	Me	**5k**	2-thienyl	2.0	**6k**	46
12	**4p**	PhCO	Me	**5a**	4-$NO_2C_6H_4$	1.5	***6l***	85
13	**4n**	MeCO	Me	**5d**	4-ClC_6H_4	10.0	**6m′**[c]	32
14	**4q**	CO_2Et	Me	**5a**	4-$NO_2C_6H_4$	5.0	—[d]	

[a] **4** (1.0 mmol), **5** (1.1 mmol), NaOH (4.0 mmol), EtOH (2.0 mL), rt, then quenched by aq HCl at 0 °C. [b] Isolated yields. [c] **6m'**:



[d] Complex mixture was obtained.

(21) For selected reviews of furan synthesis, see: (a) Kirsch, S. F. *Org. Biomol. Chem.* **2006**, *4*, 2076–2080. (b) Brown, R. C. D. *Angew. Chem., Int. Ed.* **2005**, *44*, 850–852. (c) Keay, B. A. *Chem. Soc. Rev.* **1999**, *28*, 209–215. (d) Cacchi, S. *J. Organomet. Chem.* **1999**, *576*, 42–64. (e) Hou, X. L.; Cheung, H. Y.; Hon, T. Y.; Kwan, P. L.; Lo, T. H.; Tong, S. Y.; Wong, H. N. C. *Tetrahedron* **1998**, *54*, 1955–2020.

(22) For selected examples of Paal−Knorr synthesis, see: (a) Minetto, G.; Raveglia, L. F.; Sega, A.; Taddei, M. *Eur. J. Org. Chem.* **2005**, 5277–5288, and references cited therein. (b) Minetto, G.; Raveglia, L. F.; Taddei, M. *Org. Lett.* **2004**, *6*, 389–392. (c) Lee, C.-F.; Yang, L.-M.; Hwu, T.-Y.; Feng, A.-S.; Tseng, J.-C.; Luh, T.-Y. *J. Am. Chem. Soc.* **2000**, *122*, 4992–4993.

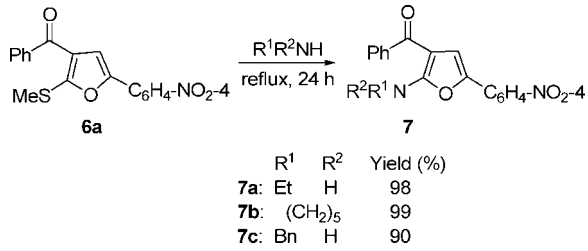
(23) For selected examples of the Feist−Benary synthesis, see: (a) Mross, G.; Holtz, E.; Langer, P. *J. Org. Chem.* **2006**, *71*, 8045–8049. (b) Holtz, E.; Langer, P. *Synlett* **2004**, 1805–1807. (c) Calter, M. A.; Zhu, C.; Lachicotte, R. J. *Org. Lett.* **2002**, *4*, 209–212.

(24) For selected examples of cycloisomerization of alkyne- and allene-containing compounds, see: (a) Dudnik, A. S.; Sromek, A. W.; Rubina, M.; Kim, J. T.; Kel'in, A. V.; Gevorgyan, V. *J. Am. Chem. Soc.* **2008**, *130*, 1440–1452. (b) Kim, S.; Lee, P. H. *Adv. Synth. Catal.* **2008**, *350*, 547–551. (c) Peng, L.; Zhang, X.; Ma, M.; Wang, J. *Angew. Chem., Int. Ed.* **2007**, *46*, 1905–1908. (d) Schwier, T.; Sromek, A. W.; Yap, D. M. L.; Chernyak, D.; Gevorgyan, V. *J. Am. Chem. Soc.* **2007**, *129*, 9868–9878. (e) Zhang, J.; Schmalz, H.-G. *Angew. Chem., Int. Ed.* **2006**, *45*, 6704–6707.

(25) For selected examples of recent advances in annulation strategies, see: (a) Kuninobu, Y.; Nishina, Y.; Nakagawa, C.; Takai, K. *J. Am. Chem. Soc.* **2006**, *128*, 12376–12377. (b) Xu, B.; Hammond, G. B. *J. Org. Chem.* **2006**, *71*, 3518–3521. (c) Zhao, L.-B.; Guan, Z.-H.; Han, Y.; Xie, Y.-X.; He, S.; Liang, Y.-M. *J. Org. Chem.* **2007**, *72*, 10276–10278. (d) Shindo, M.; Yoshimura, Y.; Hayashi, M.; Soejima, H.; Yoshikawa, Y.; Matsumoto, K.; Shishido, K. *Org. Lett.* **2007**, *9*, 1963–1966. (e) Babudri, F.; Cicco, S. R.; Farinola, G. M.; Lopez, L. C.; Naso, F.; Pinto, V. *Chem. Commun.* **2007**, 3756–3758.

(26) One example of a [3 + 2] annulation reaction toward tetrahydrofuran skeleton was reported by Junjappa and co-workers in 1988, in which a tetrasubstituted furan could be obtained in 25% overall yield by treating 2-benzoyl-3-cyano-1,1-bis(methy1thio)propenide anion with 4-chlorobenzaldehyde to yield a cyclic hemiacetal, which was further treated with $BF_3 \cdot OEt_2$ and methanol. Singh, L. W.; Ila, H.; Junjappa, H. *J. Chem. Soc., Perkin Trans. I* **1988**, 2365−2368.

SCHEME 2



EWG and ketene-*S*,*S*-acetal moieties of **4** had influence on the annulation. The reaction of **4p** with **5a** could give the desired furan **6*l*** in high yield (entry 12). In the case of **4n** and **5d**, furan **6m′** was afforded by a [3 + 2] annulation along with an aldol condensation (entry 13). However, a complex mixture was obtained when **4q** was selected as substrate under identical conditions (entry 14). All furans **6** obtained were characterized by their spectra and elemental analysis and the structure of **6** was further established by X-ray diffraction studies of **6a**.[27]

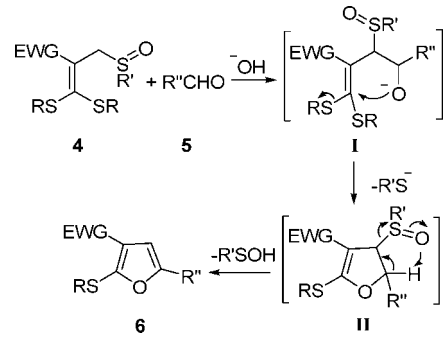
As described above, we have provided an efficient and convenient procedure for the synthesis of 2-alkylthio-3,4-disubstituted furans **6**. It is obvious that these 2-alkylthio furans can be further utilized in the synthesis of various 2-substituted furans via the direct replacement of the alkylthio group by a nucleophile. For further investigation of the application of these useful functionalized furans **6**, we explored the substitution reactions of **6a** with amines. As described in Scheme 2, 2-aminofurans **7**, which are evaluated as either a scaffold in natural product synthesis or useful building blocks in organic synthesis,[28] could be obtained in excellent yields. For example, when a mixture of **6a** (1.0 mmol) and ethylamine (3.0 mmol) was stirred in ethanol (5.0 mL) at reflux for 24 h, 2-aminofuran **7a** was produced as a white solid (98% yield). Similarly, when **6a** and piperidine or **6a** and benzylamine were subjected to the identical conditions, the desired products **7b** and **7c** were obtained in 99% and 90% isolated yields, respectively. However, when aniline was taken as the nucleophile, no reaction occurred after reacting for 48 h under identical reaction conditions and **6a** was recovered in quantitative yield.

Proposed Mechanism for the [3 + 2] Annulation. On the basis of all of the above experimental results, a possible mechanism for the [3 + 2] annulation of **4** with **5** is proposed as shown in Scheme 3. This pathway begins with an aldol condensation of functionalized sulfoxide **4** with aldehyde **5** in the presence of base to give intermediate **I**. Subsequently, an intramolecular addition−elimination reaction of **I** involving an attack of alkoxyl on ketene-*S*,*S*-acetal moiety affords dihydrofuran **II**, of which elimination of a sulfenic acid gives the target product of type **6**.

Conclusion

In summary, a set of functionalized allylic sulfides **3** have been synthesized by a thiomethylation reaction based on α-EWG ketene-*S*,*S*-acetals **1**. This three-component reaction, involving an α-EWG ketene-*S*,*S*-acetal **1**, formaldehyde, and a thiol **2**, is the first example of the Mannich-type thiomethylation of activated alkenes. Allylic sulfoxides **4** are readily obtained by a highly regioselective oxidation of the corresponding allylic sulfides **3** with use of *m*-CPBA as oxidant. Both allylic sulfides **3** and allylic sulfoxides **4** might have potential in organic synthesis due to their diverse functionalities. Thus, we explored the applications of sulfoxides **4** in the construction of polyfunctionalized furans. As a result, a [3 + 2] annulation reaction of allylic sulfoxides **4** and aldehydes **5** was uncovered. The key features of this furan synthesis are that the combination of the properties of sulfoxide (the alkylsulfinyl group is either an activating group of the adjacent methylene or a good leaving group) and ketene-*S*,*S*-acetal (substitution reaction of alkylthio group) contributes to the formation of furan scaffold and that the resulting furan derivatives, bearing a wide range of functional groups such as alkylthio, alkylamino, or carbonyl, etc., can be taken as valuable synthons for the preparation of various synthetically useful compounds. It is also of great interest to note that the presented [3 + 2] annulation gives furans in good to high yields from readily available starting materials under mild conditions. Future studies focused on the development of related transformations via the [3 + 2] annulation methodology are in progress.

SCHEME 3. Proposed Mechanism for the [3 + 2] Annulation of 4 and 5



Experimental Section

General Procedure for the Preparation of 3a−m via the Thiomethylation of 1 with Formaldehyde and Thiols (with 3d as an example). To a solution of 4,4-bis(ethylthio)but-3-en-2-one (**1d**) (190 mg, 1.0 mmol), formaldehyde (0.17 mL, 40% aqueous, 2.0 mmol), and benzylthiol (0.12 mL, 1.0 mmol) in THF (2.0 mL) was added HCl (0.17 mL, 36% aqueous, 2.0 mmol). The resulting mixture was stirred for 0.5 h at room temperature. After completion of the reaction as indicated by TLC (petrolum ether: diethyl ether = 3:1), the reaction mixture was poured into saturated aqueous NaCl (20 mL). The mixture was neutralized with aqueous Na_2CO_3 and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic phase was washed with water (3 × 20 mL), dried over $MgSO_4$, and concentrated in vacuo. The crude product was purified by flash chromatography (silica gel, petroleum ether:diethyl ether = 20:1) to give **3d** (317 mg, 97%) as a yellow oil.

3-(Benzylthiomethyl)-4,4-bis(ethylthio)but-3-en-2-one (3d). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.21 (t, J = 7.5 Hz, 3H), 1.27 (t, J = 7.5 Hz, 3H), 2.46 (s, 3H), 2.77−2.83 (m, 4H), 3.73 (s, 2H), 3.74 (s, 2H), 7.24−7.25 (m, 1H), 7.29−7.33 (m, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 203.9, 147.6, 138.1, 135.8, 129.2 (2C), 128.8 (2C), 127.4, 37.0, 34.6, 31.8, 28.3, 28.2, 15.2, 14.9. IR (KBr, cm^{-1}) 3027, 2967, 2923, 1689, 1497, 1255, 1079, 886, 704. ES-MS calcd *m*/*z* 326.1, found 365.0 [(M + 39)]$^+$. Anal. Calcd for $C_{16}H_{22}OS_3$: C, 58.85; H, 6.79. Found: C, 58.99; H, 6.70.

(27) Crystal data for **6a**: $C_{18}H_{13}NO_4S$, yellow, M = 339.35, monoclinic, space group P 21/c, a = 16.312(4) Å, b = 13.323(3) Å, c = 7.362(2) Å, V = 1599.7(7) Å^3, α = 90.00°, β = 90.00°, γ = 90.00°, Z = 4, T = 293 K, F_{000} = 704, R_1 = 0.0563, wR_2 = 0.0803.

(28) Selected examples for applications and synthesis of 2-amino furans, see: (a) Padwa, A.; Brodney, M. A.; Satake, K.; Straub, C. S. *J. Org. Chem.* **1999**, *64*, 4617–4626. (b) Nair, V.; Vinod, A. U. *Chem. Commun.* **2000**, 1019–1020. (c) Alizadeh, A.; Rostamnia, S.; Hu, M.-L. *Synlett* **2006**, 1592–1594. (d) Alizadeh, A.; Rostamnia, S.; Zoreh, N.; Oskueyan, Q. *Synlett* **2007**, 1610–1612.

Typical Procedure for the Preparation of 3e, 3i, and 3n−q via the Thiomethylation of 1, in Which 1 by Themselves Served As Thiol Sources (with 3i as an example). To a solution of 4,4-bis(ethylthio)but-3-en-2-one (**1d**) (190 mg, 1.0 mmol) and formaldehyde (0.17 mL, 40% aqueous, 2.0 mmol) in THF (2.0 mL) was added HCl (0.10 mL, 36% aqueous, 1.2 mmol). The resulting mixture was stirred for 4.5 h at room temperature. After completion of the reaction as indicated by TLC (petroleum ether:diethyl ether = 3:1), the reaction mixture was poured into saturated aqueous NaCl (20 mL). The mixture was neutralized with aqueous Na_2CO_3, and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic phase was washed with water (3 × 20 mL), dried over $MgSO_4$, and concentrated in vacuo. The crude product was purified by flash chromatography (silica gel, petroleum ether:diethyl ether = 30:1) to give **3i** (128 mg, 97%) as a yellow oil.

General Procedure for the Preparation of 4a, 4d, 4k, 4*l*, and 4n−q (with 4o as an example). To a solution of 3,3-bis(methylthio)-2-(methylthiomethyl)-1-phenylprop-2-en-1-one (**3o**) (284 mg, 1.0 mmol) in 5.0 mL of CH_2Cl_2 was added *m*-CPBA (204 mg, 1.0 mmol). The resulting mixture was stirred for 0.5 h at 0 °C. After completion of the reaction as indicated by TLC (pure diethyl ether), the reaction mixture was poured into saturated aqueous NaCl (30 mL). The mixture was neutralized with aqueous Na_2CO_3 and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic phase was washed with water (3 × 20 mL), dried over $MgSO_4$, and concentrated in vacuo. The crude product was purified by flash chromatography (silica gel, pure diethyl ether) to give **4o** (263 mg, 88%) as a yellow oil.

2-(Methylsulfinylmethyl)-3,3-bis(methylthio)-1-phenylprop-2-en-1-one (4o). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.05 (s, 3H), 2.34 (s, 3H), 2.60 (s, 3H), 4.02 (d, J = 13.0 Hz, 1H), 4.24 (d, J = 13.0 Hz, 1H), 7.43 (t, J = 7.5 Hz, 2H), 7.51 (t, J = 7.5 Hz, 1H), 7.87 (d, J = 7.5 Hz, 2H). ^{13}C NMR ($CDCl_3$ 125 MHz) δ 195.8, 147.7, 137.0, 134.1, 133.1, 129.0 (2C), 128.6 (2C), 59.4, 39.0, 17.3, 16.9. IR (KBr, cm^{-1}) 3058, 2996, 2921, 1654, 1419, 1276, 1051, 963, 797. ES-MS calcd *m*/*z* 300.0, found 323.0 [(M + 23)]$^+$. Anal. Calcd for $C_{13}H_{16}O_2S_3$: C, 51.97; H, 5.37. Found: C, 51.79; H, 5.25.

Representative Procedure for the Preparation of Furans 6 via [3 + 2] Annulation of 4 with Aldehydes 5 (with 6a as an example). To a well-stirred suspension of the corresponding 2-(methylsulfinylmethyl)-3,3-bis(methylthio)-1-phenylprop-2-en-1-one (**4o**) (300 mg, 1.0 mmol) and 4-nitrobenzaldehyde (**5a**) (166 mg, 1.1 mmol) in ethanol (2.0 mL) was added NaOH (160 mg, 4.0 mmol) at room temperature. After consumption of the starting material **4o** (TLC), the mixture was poured into saturated aqueous NaCl (20 mL). The mixture was neutralized with dilute aqueous HCl and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic phase was washed with water (3 × 20 mL), dried over $MgSO_4$, and concentrated in vacuo. The crude product was purified by flash chromatography (silica gel, petroleum ether:diethyl ether = 3:1) to give **6a** (298 mg, 88%) as a yellow solid.

(2-(Methylthio)-5-(4-nitrophenyl)furan-3-yl)(phenyl)methanone (6a). Mp 166−168 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.81 (s, 3H), 7.25 (s, 1H), 7.59 (t, J = 7.5 Hz, 2H), 7.67 (t, J = 7.5 Hz, 1H), 7.82 (d, J = 8.0 Hz, 2H), 7.90 (d, J = 7.5 Hz, 2H), 8.34 (d, J = 8.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 188.7, 160.8, 151.4, 146.4, 138.3, 135.0, 132.2, 128.5 (2C), 128.4 (2C), 124.4 (2C), 123.4 (2C), 122.6, 111.0, 13.7. IR (KBr, cm^{-1}) 2927, 1627, 1592, 1382, 1100, 889. ES-MS calcd *m*/*z* 339.1, found 340.1 [(M + 1)]$^+$. Anal. Calcd for $C_{18}H_{13}NO_4S$: C, 63.71; H, 3.86; N, 4.13. Found: C, 63.63; H, 3.91; N, 4.08.

General Procedure for the Synthesis of 7 (with 7a as an example). To a solution of (2-(methylthio)-5-(4-nitrophenyl)furan-3-yl)(phenyl)methanone (**6a**) (339 mg, 1.0 mmol) in 5.0 mL of ethanol was added ethanamine (0.20 mL, 3.0 mmol). The resulting mixture was stirred at refluxing temperature. After completion of the reaction as indicated by TLC (petroleum ether:diethyl ether = 1:1), the reaction mixture was poured into saturated aqueous NaCl (20 mL). The mixture was neutralized with aqueous $NaHCO_3$ and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic phase was washed with water (3 × 20 mL), dried over $MgSO_4$, and concentrated in vacuo. The crude product was purified by flash chromatography (silica gel, petroleum ether:diethyl ether = 3:1) to give **7a** (329 mg, 98%) as a red solid.

(2-(Ethylamino)-5-(4-nitrophenyl)furan-3-yl)(phenyl)methanone (7a). Mp 172−174 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.43 (t, J = 7.5 Hz, 3H), 3.65−3.70 (m, 2H), 7.09 (s, 1H), 7.49−7.56 (m, 3H), 7.60 (d, J = 8.5 Hz, 2H), 7.76 (d, J = 7.0 Hz, 2H), 8.21 (d, J = 8.5 Hz, 2H), 8.48 (br s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 188.3, 165.1, 145.5, 141.3, 140.0, 136.1, 131.4, 128.7 (2C), 128.1 (2C), 124.8 (2C), 122.3 (2C), 111.1, 100.3, 37.5, 15.5. IR (KBr, cm^{-1}) 3304, 2966, 2926, 1650, 1550, 1323, 1181, 1102, 739. ES-MS calcd *m*/*z* 336.1, found 337.1 [(M + 1)]$^+$. Anal. Calcd for $C_{19}H_{16}N_2O_4$: C, 67.85; H, 4.79; N, 8.33. Found: C, 67.69; H, 4.71; N, 8.25.

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Supporting Information Available: Experimental details, spectral and analytical data for compounds **3**, **4**, **6**, and **7**, copies of ^{1}H NMR and ^{13}C NMR spectra of **3**, **4**, **6**, and **7**, and crystallographic data for **6a** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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