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A convenient base-mediated synthesis of 3-aryol-4-methyl (or benzyl)-2-methylthio furans from α-oxo ketene dithioacetals and propargyl alcohols *via* domino coupling/annulations†

Xiaobing Yang,[a,b] Fangzhong Hu,*[a,b] Hongjing Di,[a,b] Xinxin Cheng,[a,b] Dan Li,[a,b] Xiaoli Kan,[a,b] Xiaomao Zou[a,b] and Qichun Zhang*[c]

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A convenient base-mediated strategy to synthesize 3-aryol-4-methyl (or benzyl)-2-methylthio furans **2** (trisubstituted furans) has been developed through the domino coupling/annulations between available α-oxo ketene dithioacetals **1** and propargyl alcohols. In this strategy, these types of bases play an important role in driving the domino coupling reaction of propargyl alcohols and further intramolecular annulations to realize the target compounds. The possible mechanism for the formation of the various products is believed to involve the generation of allenes **7**, followed by intramolecular annulations.

Introduction

α-Oxo ketene dithioacetals (β,β-bis(alkylthio)-α,β-enones) are highly functionalized α,β-unsaturated carbonyl intermediates, which can undergo a variety of transformations.[1] Generally, the reaction centers in α-oxo ketene dithioacetals could be the carbonyl group, the double bond, or sulfur atoms, and deprotonation can occur at several sites, which really depend upon the structure of the α-oxo ketene dithioacetals.[1c] The presence of two β-alkylthio substituents in α-oxo ketene dithioacetals affords a higher level of oxidation in manipulation of functional groups and in many cases, generates a product containing an S-functionalized group, which can be further employed in additional synthetic transformations.[1a] Numerous one-pot transformations, involving a cascade of 1,2- and 1,4-nucleophilic addition reactions to α-oxo ketone dithioacetals, have been widely employed to synthesize a variety of heterocyclic compounds, suggesting that α-oxo ketene dithioacetal compounds can act as an extremely versatile three-carbon synthon for the manipulation of functional groups and the construction of C–C bonds.[1b] Elaborations on an α-oxo ketene dithioacetal skeleton, particularly on those involving the C–C bond formation with various carboelectrophiles (aldehydes, simple ketones, enones, alcohols), would provide an efficient linkage between ketene dithioacetal functionality and a variety of other functional groups that have shown promising properties for applications.[1a,b]

Highly substituted furans play an important role as structural elements in many biologically active natural molecules, pharmaceutics (*e.g.*, ranitidine or zantac), and functional macromolecules.[2] Moreover, they are useful intermediates in synthetic organic chemistry.[3] So developing novel synthetic routes toward the formation of polysubstituted furan rings is very important.[4] Among the reported approaches to multiply substituted furans,[5] cycloisomerizations of alkynyl ketones catalyzed by transition metals are particularly attractive.[6] This method could be further developed using allenyl ketones as starting materials and Rh(I),[6a,b] Ag(I),[6c,d] Au(III),[6e,f,g] or Pd-(0/II)[6h,i,j] complexes as catalysts for 5-*endotrig* cyclizations. Although transition-metal-catalyzed cyclization is very convenient to prepare trisubstituted furans,[7] there are some drawbacks in this type of cyclization process: (a) transition-metal reagents are normally expensive, poisonous, and environmentally unfriendly; (b) the starting materials are generally difficult to obtain so that transition-metal-catalyzed cyclization has limited practical applications. Recently, transition-metal-free processes for the formation of C–C, C–N, C–O and C–S bonds have become an important field.[8] Considering the environmental friendliness and atom-economical purpose, developing a new system for the synthesis of functionalized and polysubstituted furans should be a promising and attractive route. In this context, we will present a convenient base-mediated protocol for the intramolecular cyclization of α-oxo ketene dithioacetals and propargyl alcohols to generate 2,3,4-trisubstituted furans at room temperature.

[a]*State Key Laboratory and Institute of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, China*
[b]*Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300071, China*
[c]*School of Materials Science Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore. E-mail: fzhu@nankai.edu.cn, qczhang@ntu.edu.sg*
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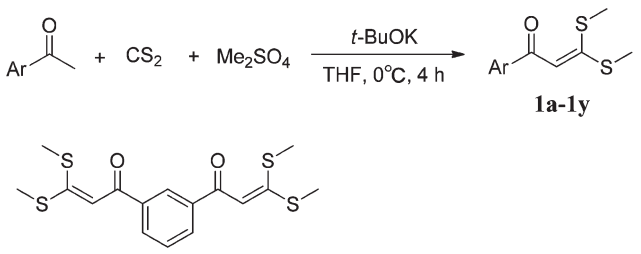
Results and discussion

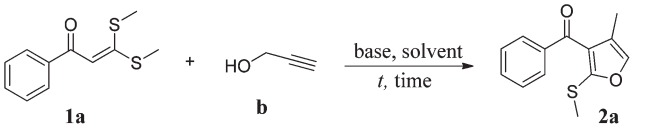
Initially, the starting α-oxo ketene dithioacetals were prepared *via* the reaction of the corresponding aryl or heteroaryl ethyl ketones with carbon disulphide in the presence of potassium *tert*-butoxide, followed by methylation with dimethylsulfate (Scheme 1).[9]

Next, 3,3-bis (methylthio)-1-phenyl-2-propen-1-one **1a** and propargyl alcohol **b** were chosen as model substrates for the initially-attempted new cascade processes in the presence of *t*-BuOK in THF. It was found that the combination of 1 equiv. of **1a**, 1.2 equiv. of **b** and 2.2 equiv. of *t*-BuOK afforded only traces of the furan product **2a** after stirring at room temperature (RT) and 60 °C for 10–24 h (Table 1, entries 1 and 2). Most of the starting material could be recovered. When the amount of *t*-BuOK was increased to 1.2 equiv., the desired furan **2a** was obtained in 13–15% yield (Table 1, entries 3 and 4). This result encouraged us to screen suitable reaction conditions for this type of reaction. It is noteworthy to point that both 2.2 equiv. of **b** and *t*-BuOK furnished the furan product **2a** in 65% yield after stirring at RT for 4 h (Table 1, entry 6). Continuously increasing the amount of both **b** and *t*-BuOK resulted in lower yield (Table 1, entry 8). The yields also became lower when the reaction temperature was increased from room temperature to 60 °C (Table 1, entries 5, 6, 9 and 10). Interestingly, the reaction could proceed at even lower temperature (0 °C), however, a long time (normally, several days) is required in order to achieve a complete conversion (Table 1, entry 7). Other alkali metal bases such as *t*-BuONa and CH_3ONa have poor performance in this type of reaction (Table 1, entries 11 and 12). Soluble amine bases such as DBU and Et_3N have also been tried, however, none of them could kick this type of reaction going (Table 1, entry 13). When the base *t*-BuOK was replaced by NaH, the yield decreased to 30% (Table 1, entry 10). Changing the solvents to dioxane or toluene, slightly decreased yields were obtained (Table 1, entries 14 and 15). However, if other solvents such as CH_2Cl_2, DMF, Et_2O, CH_3CN and DMSO were employed, a poor reaction yield was observed (Table 1, entries 16–20).



Scheme 1 Starting materials of **1a–1y**. **1a**: Ar = C_6H_5; **1b**: Ar = 4-FC_6H_4; **1c**: Ar = 4-ClC_6H_4; **1d**: Ar = 4-BrC_6H_4; **1e**: Ar = 4-IC_6H_4; **1f**: Ar = 4-MeC_6H_4; **1g**: Ar = 4-*tert*-BuC_6H_4; **1h**: Ar = 4-phenyl–phenyl; **1i**: Ar = 4-$MeOC_6H_4$; **1j**: Ar = 4-$PhOC_6H_4$; **1k**: Ar = 2-MeC_6H_4; **1l**: Ar = 2-$MeOC_6H_4$; **1m**: Ar = 3-FC_6H_4; **1n**: Ar = 3-$CF_3C_6H_4$; **1o**: Ar = 3-acetylC_6H_4; **1p**: Ar = 3-MeC_6H_4; **1q**: Ar = 3-$MeOC_6H_4$; **1r**: Ar = 2-furyl; **1s**: Ar = 2-(5-mefuryl); **1t**: Ar = 2-thienyl; **1u**: Ar = 1-naphthyl; **1v**: Ar = 3,4-$Cl_2C_6H_3$; **1w**: Ar = benzo[*d*][1,3]dioxol-3-yl; **1x**: Ar = 3,4-$Me_2C_6H_3$.

Table 1 Optimized reaction conditions for synthesis of **2a**[a]

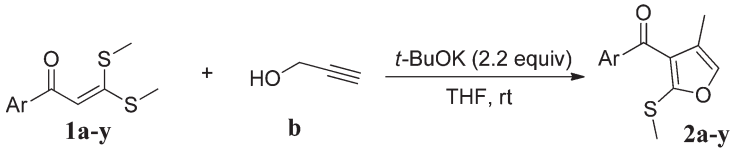


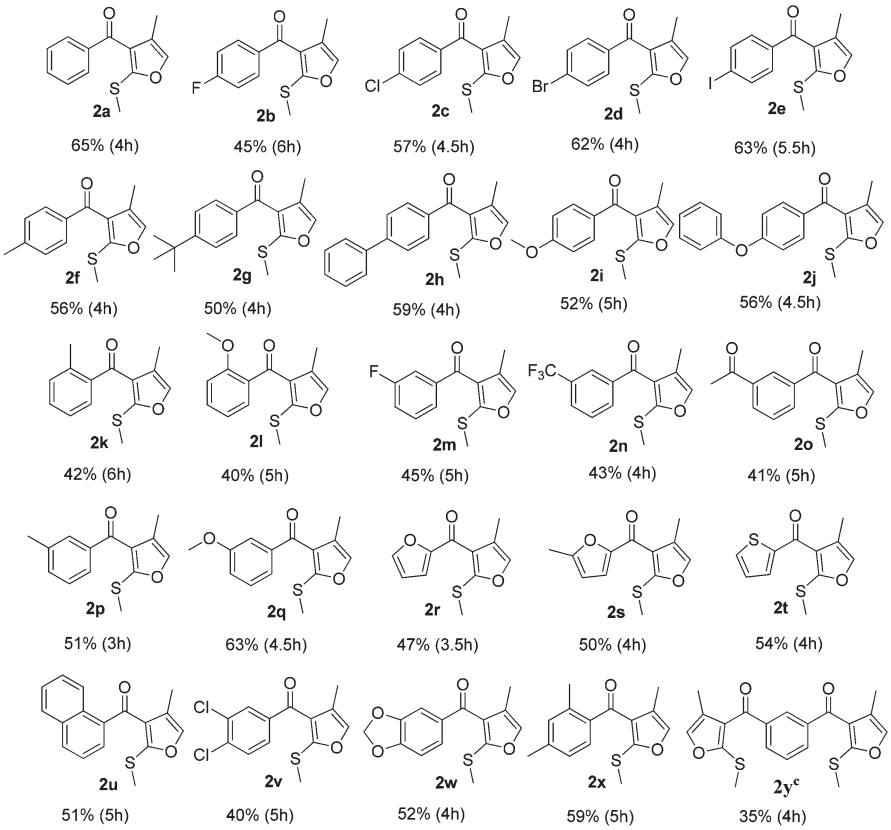
Entry	**b** (equiv.)	Base (equiv.)	Solvent	Temp (°C)	Time (h)	Yield[b] (%)
1	1.2	*t*-BuOK (2.2)	THF	60	10	Traces
2	1.2	*t*-BuOK (2.2)	THF	rt	24	Traces
3	1.2	*t*-BuOK (1.2)	THF	60	10	15
4	1.2	*t*-BuOK (1.2)	THF	rt	15	13
5	2.2	*t*-BuOK (2.2)	THF	60	2	38
6	2.2	*t*-BuOK (2.2)	THF	rt	4	65
7	2.2	*t*-BuOK (2.2)	THF	0	60	50
8	3.2	*t*-BuOK (3.2)	THF	rt	3	40
9	2.2	NaH (2.2)	THF	60	2	10
10	2.2	NaH (2.2)	THF	rt	20	30
11	2.2	*t*-BuONa (2.2)	THF	rt	2	50
12	2.2	CH_3ONa (2.2)	THF	rt	20	12
13	2.2	DBU (2.2)	THF	rt	24	s.m.[c]
14	2.2	*t*-BuOK (2.2)	Dioxane	rt	2	50
15	2.2	*t*-BuOK (2.2)	Toluene	rt	6	45
16	2.2	*t*-BuOK (2.2)	CH_2Cl_2	rt	10	12
17	2.2	*t*-BuOK (2.2)	DMF	rt	24	s.m.[c]
18	2.2	*t*-BuOK (2.2)	Et_2O	rt	6	20
19	2.2	*t*-BuOK (2.2)	CH_3CN	rt	2	Traces
20	2.2	*t*-BuOK (2.2)	DMSO	rt	2	25

[a] Reaction conditions: **b** and base were stirred in 10 mL of solvent at rt under N_2 for 15 min, followed by addition of **1a** (0.5 mmol, 1.0 equiv.). [b] Isolated yield after silica gel column chromatography. [c] s.m. = starting material.

With the optimized reaction conditions in hand, we examined the substrate scope of this strategy for the synthesis of 2,3,4-trisubstituted furans using a variety of α-oxoketene dithioacetals and propargyl alcohol, and the results are shown in Table 2. We first investigated the electronic effects of substituents in different positions on the aryl ring. It was found that *para*-substituents of the aromatic ring with stronger electron-withdrawing groups such as fluoro and chloro delivered relatively lower yields compared to those with weak electron-withdrawing groups such as bromo, iodo, phenyl and hydrogen (**2a–2e** and **2h**). Electron-withdrawing groups in the *meta*-position (**1m–1o**) gave the corresponding furans in moderate yields of 45–41%. These results indicated that electron-withdrawing groups on the benzene ring to some extent were slightly unfavorable for the reaction. In contrast, substrates with various electron-donating groups in the *para*-substituted position, such as methyl, *tert*-butyl, methoxy and phenoxy (**1f**, **1g**, **1i** and **1j**) provided products in relatively high yields. *ortho*-Substituted substrates with a methyl or a methoxy group produced **2k** or **2l** in only 42% or 40% yield. Substrate **1p** bearing the methyl group at the *meta*-position furnished **2p** in 51% yield. Compound **1q**, in which the *meta*-position is carried with a methoxy group, was smoothly cyclized producing **2q** in good yield. The Ar of the starting materials could also be heteroaryl groups, such as 2-furyl (**1r**), 2-(5-mefuryl) (**1s**), and 2-thienyl (**1t**), furnishing **2r**, **2s**, and **2t** in 47, 50 and 54% yields, respect-

Table 2 Synthesis of 3-substituted-4-methyl-2-methylthio-furan derivatives[a,b]





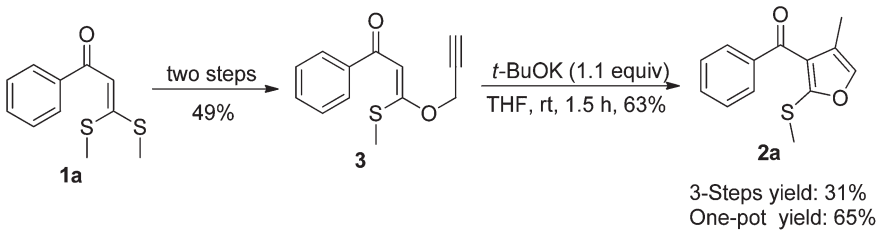
[a] Reaction conditions: the mixture of **b** (1.1 mmol, 2.2 equiv.) and *t*-BuOK (1.1 mmol, 2.2 equiv.) was stirred in 10 mL of THF at rt under N_2 for 15 min, followed by addition of **1** (0.5 mmol, 1.0 equiv.) at room temperature. [b] Isolated yield after silica gel column chromatography. [c] **b** (2.2 mmol, 4.4 equiv.) and *t*-BuOK (2.2 mmol, 4.4 equiv.) were used.

ively. Naphthyl-substituted substrate **1u** gave a good result. In addition, substrates with various polysubstituents (**1v–1x**) were also tested, and in most cases, satisfactory yields of the corresponding cyclized products were achieved. Interestingly, the difuran product **2y** can also be obtained from the treatment of **1y** and propargyl alcohol in 35% yield.

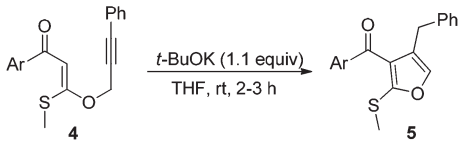
It is interesting to note that the stepwise process leading to the formation of 2,3,4-trisubstituted furans was found to be far less efficient than the one-pot process (Scheme 2). In a separate reaction, propargyl alcohol adduct **3**[10] was separated *via* dimethylsulfonium perchlorate salt[11] and subjected to 1.1 equiv. of *t*-BuOK. Furan **2a** was obtained in 31% overall yield from α-oxo ketene dithioacetal **1a**, while the same product was obtained in 65% yield from **1a**, highlighting the distinct advantage of the one-pot domino process.

Under the standard conditions for the cyclization, the reaction between **1a** and 3-phenylpropargyl alcohol **c** only produced 10% yield of the corresponding cyclized product **5a**. Interestingly, the *O*,*S*-acetal intermediates **4** can afford **5** in yields ranging from 40 to 67% in the presence of 1.1 equiv. of *t*-BuOK (Scheme 3). However, no desired product was obtained if 2-butyn-1-ol or 3-butyn-2-ol was employed to react with **1a** in the presence of *t*-BuOK in THF.

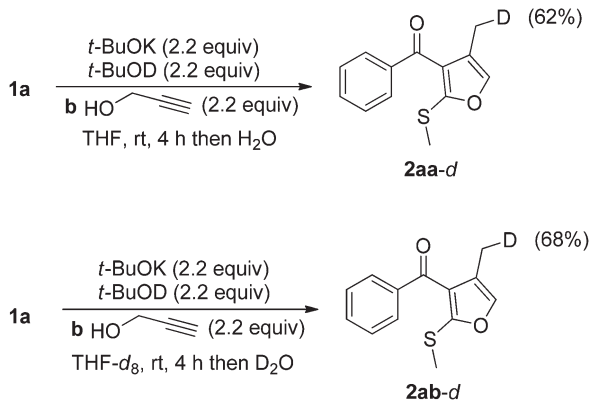
The suggested reaction mechanism is shown in Scheme 4. The cyclization between **1a** and propargyl alcohol **b** was carried out in the presence of *t*-BuOK in THF with 2.2 equiv. of *t*-BuOD. After completion of the reaction, the mixture was quenched with H_2O, followed by the usual workup and purification. Product **2aa**-*d* was obtained with 62% deuterium incorporated at the $-CH_3$ group of the furan ring. A similar level of deuterium incorporation product **2ab**-*d* was observed when the reaction was performed employing *t*-BuOK and *t*-BuOD in THF-d_8 followed by quenching with D_2O. These results suggested that the reaction might undergo the intermediate **8** containing anions generated from the deprotonation of **1a** by *t*-BuOK and the hydrogen of the C=C double bond in **1a** is the



Scheme 2 An alternative method for the synthesis of **2a**.



Scheme 3 Synthesis of **5** from the intermediates **4**. Ar = C_6H_5 (**5a**, yield: 55%); Ar = 4-ClC_6H_4 (**5b**, yield: 67%); Ar = 4-MeC_6H_4 (**5c**, yield: 60%); Ar = 2-furyl (**5d**, yield: 40%); Ar = 1-naphthyl (**5e**, yield: 63%).

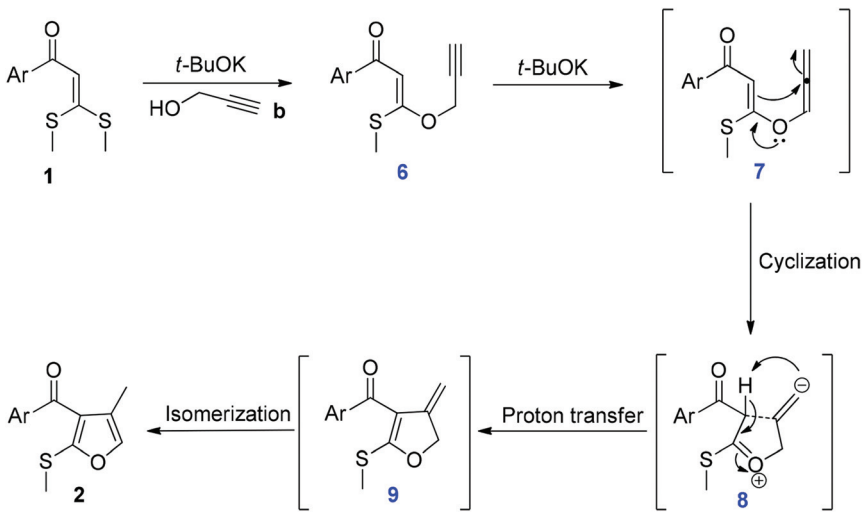


Scheme 4 Deuteration experiments.

source of protonation at the $-CH_3$ group at the 4th position of the furan ring (**2a**).

On the basis of the deuteration experiments, the mechanism for the reactions between α-oxo ketene dithioacetals and propargyl alcohols is proposed in Scheme 5. Firstly, deprotonation of propargyl alcohol **b** by *t*-BuOK gave the propargyloxyanion, which undergoes the Michael addition reaction with **1** to form the *O*,*S*-acetal intermediate **6**, followed by generation of allene **7** in the presence of excess *t*-BuOK rather than the involvement of the Claisen-rearrangement reaction.[10b] After an intramolecular nucleophilic attack on the intermediate allene **7**, the cyclization product **8** is formed, whose proton at the C-3 position is transferred intramolecularly to furnish **9**. The final product **2** was obtained through the isomerization of **9**.

In conclusion, a convenient base-mediated strategy has been developed for the synthesis of trisubstituted furans through the reaction between α-oxo ketene dithioacetals and propargyl alcohol *via* domino coupling/annulations. The cyclization reactions are promoted by *t*-BuOK and could have occurred in THF at room temperature. Many functional groups have been tried to produce a wide range of synthetically relevant furans. The easy accessibility of the starting materials, simplicity of execution and mild reaction conditions should make this new strategy more convenient for research and application.



Scheme 5 Proposed mechanism of the domino coupling/annulations.

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