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Iodine-Mediated Copper-Catalyzed Efficient α-C(sp^2)-Thiomethylation of α-Oxoketene Dithioacetals with Dimethyl Sulfoxide in One Pot

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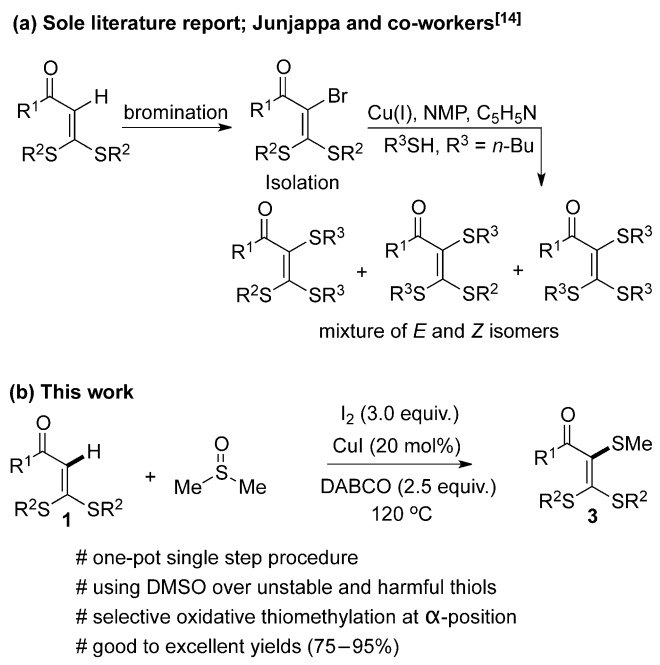
Abstract: The direct α-Csp^2–H functionalization and thiomethylation of α-oxoketene dithioacetals (DTAs) has been accomplished with dimethyl sulfoxide (DMSO) in the presence of iodine and a copper(I) salt for the first time. A prerequisite is the *in situ* iodination of the α-Csp^2 atom of dithioacetals that could offer other reaction channels. The operationally simple one-pot protocol includes region-defined consecutive iodination and sulfenylation of the challenging α-Csp^2–H bond of dithioacetals employing cheap and readily available reagents. DMSO here plays a dual role as thiomethyl source and solvent.

Keywords: cascade reaction; 1,4-diazabicyclo[2.2.2]octane (DABCO); dimethyl sulfoxide (DMSO); iodination; thiomethylation

Introduction

The introduction of the thioalkyl group into a chemical species is a fundamentally important process in organic synthesis.[1] The direct and selective thioalkylation of Csp^2–H bond of internal olefins is one of the most versatile approaches for the construction of thioalkylated compounds. During past decades, thioalkylation of various organic species has been achieved employing sulfonyl hydrazides,[2] disulfides,[3] sulfenamides[4] and thiols.[5] Although the above reagents successfully insert the thioalkyl group, they suffer from incomparable difficulties such as typical handling of the reagents, harsh conditions, poor yield, and tedious work-up procedure. From a practical perspective, the synthesis of important motifs by thioalkylation with cheaper reagents and easy operation is highly desirable. In this context, the new candidate is dimethyl sulfoxide (DMSO), an inexpensive and low-toxic polar aprotic solvent, which has been widely used in organic synthesis. Moreover, being an effective polar reaction medium, DMSO also been utilized as a oxidant in the well-known reactions such as Swern oxidation,[6] Pfitzner–Moffatt oxidation,[7] Corey–Chaykovsky epoxidation, cyclopropanation[8] and Kornblum reaction.[9] Furthermore, DMSO serves as a multipurpose precursor for the O, CH_2SMe, Me, CN, and CHO units.[10] However, DMSO as a thiomethyl source was rarely exploited.[11] Recently, Li et al. and Gao and co-workers[12] employed DMSO as a source of thiomethyl groups for the synthesis of α-alkoxy methyl sulfides and thiomethylated heterocycles, respectively.

During the past few years, we have explored polarized olefins in the form of α-oxoketene dithioacetals (DTAs) as key precursor for the synthesis of numerous heterocycles.[13] This time, we envisioned to functionalize the sterically hindered and electron rich α-Csp^2–H bond of DTAs by the thiomethyl group, which has seldom been explored. It is worth mentioning that the only disclosure of the thiomethylation of dithioacetals was reported by Junjappa et al.[14] *via* a two-step process employing thiols as alkyl sulfide agent (Scheme 1a). However, the reported strategy suffers from low selectivity, expensive reagents, harsh conditions, and a multistep reaction procedure. Functionalization of an internal olefinic C–H bond has been a challenging task in organic synthesis due to the intrinsic steric hindrance and electronic environment around the carbon-carbon double bond. It has



1a: R ^{1}= C $_6H_5$; **1b**: R ^{1} = 4-MeC_6H_4; **1c**: R ^{1}= 4-MeOC_6H_4 **1d**: R^1 = 4-ClC_6H_4; **1e**: R^1 = 4-BrC_6H_4; **1f**: R^1 = 3,4-$OCH_2OC_6H_3$; **1g**: R^1 = 2-naphthyl; **1h**: R ^{1} = biphenyl; **1i**: R ^{1} = 2-furyl; **1j**: R ^{1} = 2-thienyl; **1k:** R^1 = 4-MeOC_6H_4CH=CH; **1l:** R^1 = $(Me)_3C$; R^2 = Me for **1a-l**; **1m**: R^1 = C_6H_5; **1n**: R^1 = 3-MeOC_6H_4; **1o**: R^1 = 4-$CF_3C_6H_4$; **1p**: R^1 = 2-naphthyl; **1q**: R^1 = 2-furyl; **1r**: R^1 = 2-thienyl; R^2 = Et for **1m–r**; **1s**: R^1 = C_6H_5; **1t**: R^1 = 4-MeC_6H_4; **1u** R^1 = 2-thienyl; R^2 = *n*-Pr for **1s-u**; **1v**: R^1 =4-MeOC_6H_4, **1w:** R^1 = 2-ClC_6H_4; R^2 = *n*-Bu for **1v, w.**

Scheme 1. Thiomethylation of α-oxoketene dithioacetals (DTAs).

been reported that replacement of the H of C*sp*^{2}–H by a thioalkyl group, first requires activation followed by coupling with a suitable thioalkyl source.[15] One of the significant ways to activate the internal olfenic C*sp*^{2}–H bond is *in situ* iodination followed by oxidative coupling.[16]

It is envisioned that if the selective iodination of C*sp*^{2}–H bond of DTAs is feasible by molecular iodine, then *in situ* oxidation of the carbon-iodine bond could generate a transition metal complex intermediate primed for selective thiomethylation by DMSO. As a proof of our concept, we successfully achieved this goal and report here a highly efficient and effective one-pot direct thiomethylation of α-oxoketene dithioacetal with DMSO *via* iodine-mediated Cu(I) catalysis in a tandem fashion (Scheme 1b). This strategy provides a powerful and general route to activate the sterically hindered C*sp*^{2}–H bond of DTAs, which could be further functionalized to privileged and prevalent motifs for various purposes.

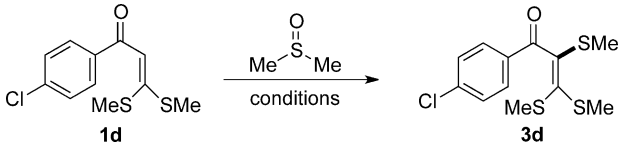
Results and Discussion

To test the above hypothesis, the present study was initiated with 1-(4-chlorophenyl)-3,3-bis(thiomethyl)-prop-2-en-1-one **1d** (1.0 mmol) as model substrate in DMSO (5 mL) under varying conditions and the results are listed in Table 1. The above model reaction was performed with iodine (1 equiv.) and K_2CO_3 (2 equiv.) at room temperature, no trace of the desired product was obtained even after 48 h (Table 1, entry 1). Literature reports indicate that the generation of the thiomethyl unit from DMSO requires high temperatures. Therefore, next we carried out the above reaction at 120 °C. Only traces of the desired product were obtained after 48 h of heating (Table 1, entry 2). Next, increasing the amount of I_2 also could not provide a satisfactory result (Table 1, entries 3 and 4). In an effort to improve the efficiency of the reaction, we performed the reaction in the presence of CuI and the ligand 1,4-diazabicyclo[2.2.2]octane (DABCO) (10 mol% each). To our pleasure, the desired product was obtained in 50% yield (Table 1, entry 5). Increasing the amount of CuI and DABCO improved the yield to 75% (Table 1, entry 6). Further increments in the loading of CuI and DABCO did not improve the result (Table 1, entry 7).

The success of this protocol prompted us to investigate some other copper salts such as CuCl and CuBr, which could not provide any better results (Table 1, entries 8 and 9).The use of Cs_2CO_3 in place of K_2CO_3 afforded a similar result (Table 1, entry 10). From our experiences, we assumed that the ligand DABCO may also act as base. Consequently, the use of 2 equiv. of DABCO without an inorganic base in the above reaction provided the desired product in 80% yield (Table 1, entry 11). Finally, we optimized the loading of DABCO, and it was found that 2.5 equiv. of DABCO furnished the best result (Table 1, entries 12 and 13). Utilization of $Cu(OAc)_2$ instead of CuI could not provide a better result (Table 1, entries 14 and 15). To observe the efficiency of iodine as a reagent as well as oxidizing agent, we used some other oxidizing agents like NBS and $Cu(OAc)_2$ with iodine. All these studies indicated that 3 equiv. of iodine was suitable for this conversion (Table 1, entries 16 and 17). Increasing the temperature did not improve the result (Table 1, entry 18) and at low temperature i.e., 100 and 80 °C the iodized product could not be fully converted to the thiomethylated product even after 24 h (Table 1, entries 19 and 20).

During our optimization of the loading of iodine, it was found that the reaction was completed within 24 h when we used 3 equiv. of iodine. Increasing the amount of iodine further did not provide any significant change in the result and with less iodine a significant decrease in yield was observed (Table 1, entries 21 and 22). Control reactions in the absence of I_2

Table 1. Optimization of the reaction conditions.[a]



Entry	I_2 (equiv.)	Oxidizing agent (equiv.)	Base (equiv.)	DABCO (equiv.)	Catalyst (equiv.)	Temp. [°C]/Time [h]	Yield [%][c]
1	(1)	none	K_2CO_3 (2)	none	none	r.t./48	none
2	(1)	none	K_2CO_3 (2)	none	none	120/48	trace
3	(2)	none	K_2CO_3 (2)	none	none	120/48	trace
4	(3)	none	K_2CO_3 (2)	none	none	120/48	10
5	(3)	none	K_2CO_3 (2)	(0.1)	CuI (0.1)	120/24	50
6	(3)	none	K_2CO_3 (2)	(0.2)	CuI (0.2)	120/24	75
7	(3)	none	K_2CO_3 (2)	(0.3)	CuI (0.3)	120/24	75
8	(3)	none	K_2CO_3 (2)	(0.2)	CuCl (0.2)	120/24	60
9	(3)	none	K_2CO_3 (2)	(0.2)	CuBr (0.2)	120/24	65
10	(3)	none	Cs_2CO_3 (2)	(0.2)	CuI (0.2)	120/24	75
11	(3)	none	none	(2.0)[b]	CuI (0.2)	120/24	80
12	**(3)**	**none**	**none**	**(2.5)[b]**	**CuI (0.2)**	**120/24**	**85**
13	(3)	none	none	(3.0)[b]	CuI (0.2)	120/24	85
14	(3)	none	none	(2.5)[b]	$Cu(OAc)_2$ (0.1)	120/30	75
15	(3)	none	none	(2.5)[b]	$Cu(OAc)_2$ (0.2)	120/24	75
16	(2)[d]	NBS (1)	none	(2.5)[b]	CuI (0.2)	120/24	50
17	(1)	$Cu(OAc)_2$ (2)	none	(2.5)[b]	CuI (0.2)	120/24	60
18	(3)	none	none	(2.5)[b]	CuI (0.2)	140/24	80
19	(3)	none	none	(2.5)[b]	CuI (0.2)	100/24	60
20	(3)	none	none	(2.5)[b]	CuI (0.2)	80/24	40
21	(4)	none	none	(2.5)[b]	CuI (0.2)	120/24	85
22	(2)	none	none	(2.5)[b]	CuI (0.2)	120/24	70
23	none	none	none	(2.5)[b]	CuI (0.2)	120/24	none

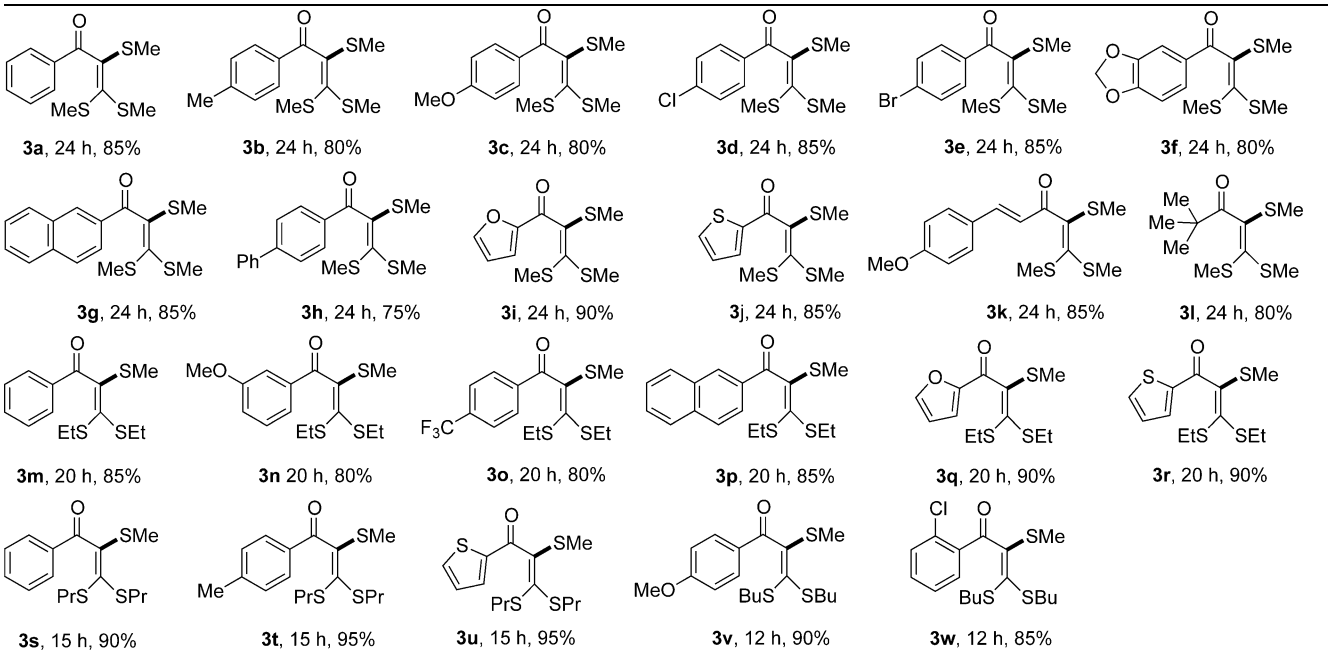
[a] *Reaction conditions:* All reactions were performed with **1d** (1.0 mmol), I_2 (3.0 equiv.), CuI (20 mol%), DABCO (2.5 equiv.), DMSO (5 mL) in the open atmosphere.
[b] DABCO acts both as a base and ligand.
[c] Isolated yield.
[d] α-Brominated product was obtained in 20% yield.

did not proceed at all indicating that molecular iodine is essential for this cascade reaction (Table 1, entry 23). Thus, **1d** (1.0 mmol), I_2 (3.0 equiv.), CuI (20 mol%), DABCO (2.5 equiv.), DMSO (5 mL) at 120 °C was found to represent the optimal reaction conditions, which provided **3d** in 85% yield (Table 1, entry 12).

With the optimized reaction conditions in hand, the generality and scope of the molecular iodine-mediated copper-catalyzed direct thiomethylation of the α-Csp^2–H bond of α-oxoketene dithioacetals was next explored. To our satisfaction, the results indicated that dithioacetals bearing diverse functional groups and substitution patterns afforded the desired products in good to excellent yields (Table 2, up to 95%). In general, electron-neutral (**1a**, **1b**), electron-donating (**1c**, **1f**, **1k**, **1l**) and electron-withdrawing (**1d**, **1e**) α-oxoketene dithioacetals were successfully converted to their corresponding thiomethylated products in 80–85% yields. The electronic and steric nature of the aromatic ring of α-oxoketene dithioacetals had no obvious influence on the reaction efficiency (**3a–j**).

Sterically hindered extended aromatics (**1g**, **1h**) and heteroaromatics (**1i**, **1j**) as R^1 substituents of dithioacetals did not disturb the outcome of the reaction, and afforded the desired products in good to excellent yields (Table 2, **3g–j**). However, when the chain length at the sulfur atom was augmented from methyl to ethyl, propyl, and *n*-butyl a significant lowering in the reaction time was observed. In the case of ethyl, the reaction was completed within 20 h (**3m–r**). In the case of propyl and *n*-butyl groups, the reactions were completed within 15 h (**3s–u**) and 12 h (**3v**, **w**), respectively. This lowering in time upon increasing the length of the thioalkyl group may be due to enhanced electron density at the α-carbon of long chain thioalkyl substituents, which further boosts the rate of the *in situ* iodination reaction (first step of the reaction). Our all efforts for the thiomethylation of α-oxoketene

Table 2. Scope of α-oxoketene dithioacetals **1**.

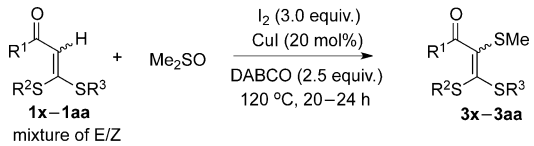


dithioacetals containing R^1 as methyl and R^2 as benzyl were futile.[17]

To illustrate the broad synthetic utility and generality of our developed one-pot cascade reaction, we further investigated various unsymmetrical dithioacetals (both sulfur atoms being differently substituted) under the optimized conditions (Scheme 2, **1x–1aa**). Remarkably, all these unsymmetrical dithioacetals were tolerated well, and the reactions proceeded smoothly providing the desired products (**3x–3aa**) as inseparable mixtures of *E*/*Z* isomers in 80–90% yields (Scheme 2).

Our all efforts to separate these *E*/*Z* isomers were futile. The structures of all the newly synthesized compounds **3x–3aa** were elucidated by their satisfactory spectral (IR, ^{1}H, ^{13}C NMR and HR-MS) studies.

To have a deeper understanding into the reaction process, we performed the thiomethylation of **1f** under the optimized reaction conditions followed by the segregation of products at different intervals, that were monitored by ^{1}H NMR (Scheme 3). After 10 h,

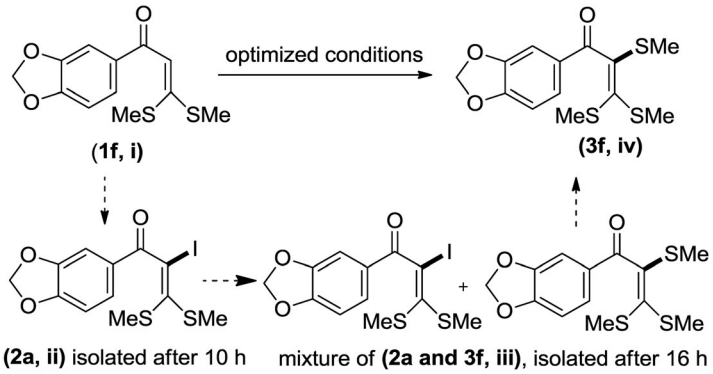


3x: R^1 = 4-ClC_6H_4, R^2 = Me, R^3 = Et (24 h, 90%)
3y: R^1 = biphenyl, R^2 = Me, R^3 = *n*-Pr (20 h, 90%)
3z: R^1 = 4-MeOC_6H_4, R^2 = Me, R^3 = *n*-Pr (20 h, 85%)
3aa: R^1 = naphthyl, R^2 = Me, R^3 = Et (24 h, 80%)

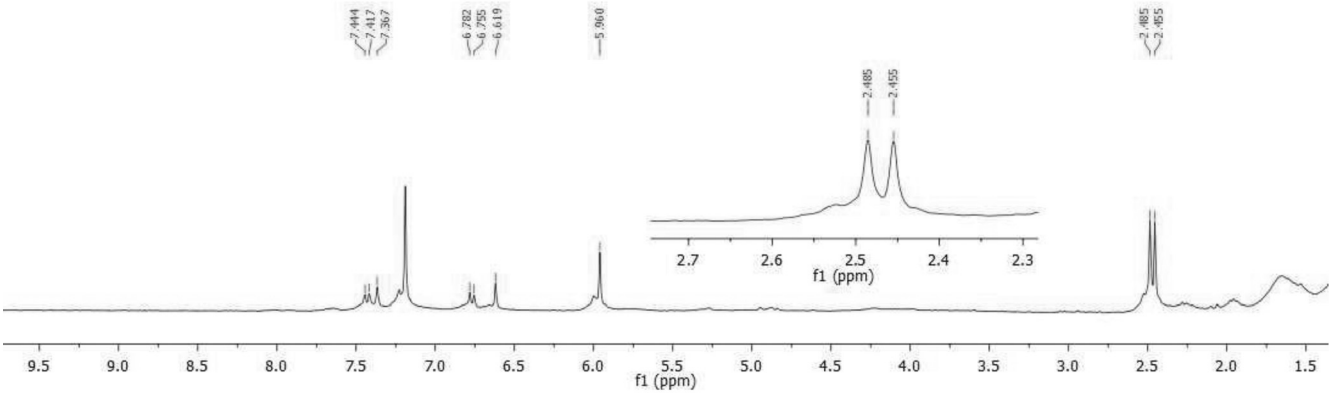
Scheme 2. Region-defined thiomethylation of unsymmetrical dithioacetals.

the reaction afforded the α-iodo derivative **2a** suggesting that the first step of the reaction is iodination of the dithioacetal. The formation of **2a** is supported by disappearance of the α-H peak in the ^{1}H NMR at 6.61 ppm, while methyl peaks of SMe of the parent dithioacetal **1f** shifted up field from 2.45 and 2.48 ppm to 2.16 and 2.47 ppm (i) and (ii). An HR-MS study also supported the formation of **2a**. Next, we analyzed the reaction after 16 h. The ^{1}H NMR study showed a mixture of **2a** and our desired product **3f** with clear appearance of SMe peaks at 2.12, 2.13 and 2.42 ppm together with the parent SMe peaks at 2.17 and 2.48 ppm (iii). The above results suggest that **2a** slowly converts into the desired product **3f**. Finally, we stopped the reaction after complete conversion of **2a** into **3f** (monitored through TLC), and work-up of the reaction mixture furnished the desired product **3f** in 80% yield (iv).

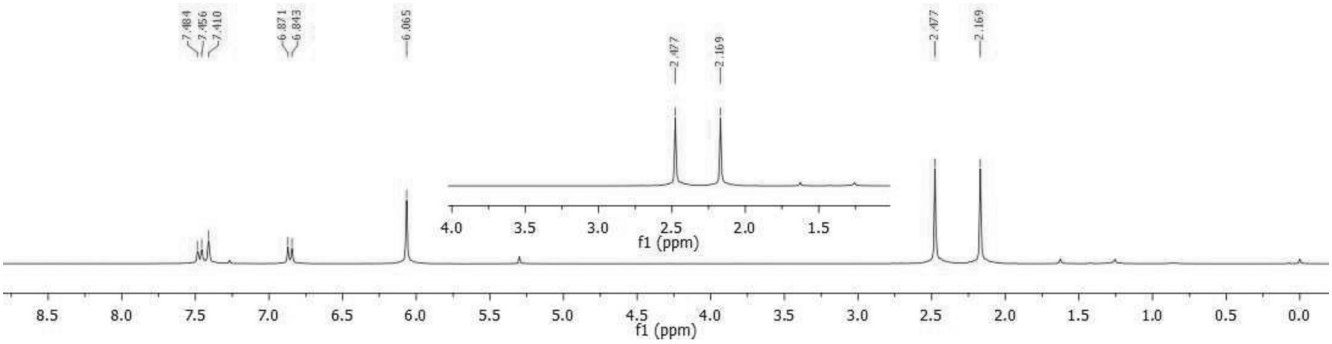
To gain some more insights into the mechanism of the reaction, a series of control experiments was performed. The isolated iodo derivative **2a** was treated under the optimized conditions. Notably, **2a** was converted quantitatively to the desired product **3f** within 14 h. These results clearly confirmed the intermediacy of **2a** in the tandem thiomethylation of dithioacetal **1f** [Eq. (1)]. To prove the formation of methanethiol from DMSO, we performed the thioalkylation of **1j** with a mixture of DMSO, EtSSEt and EtSH. This reaction leads the formation of **3j** in 45% yield with selective formation of the α-thioethylated product **4** in 30% yield [Eq. (2)]. To further improve the efficiency of the above reaction, we performed the thioethylation of **1j** with EtSSEt and EtSH independently.



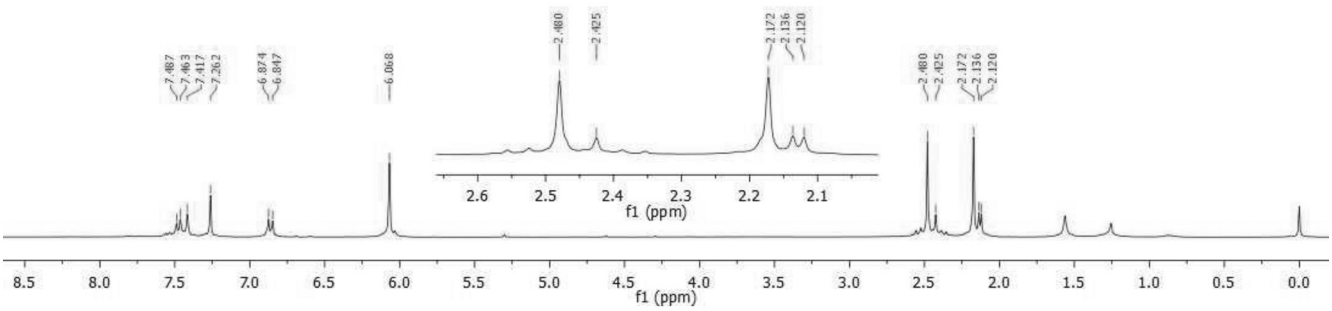
(i)



(ii)

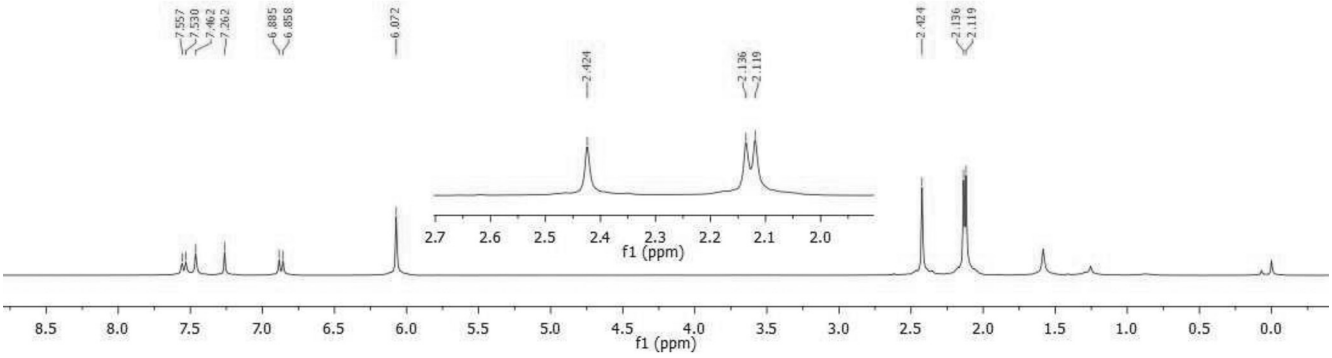


(iii)



Scheme 3. Determination of the reaction pathway by ^{1}H NMR.

(iv)

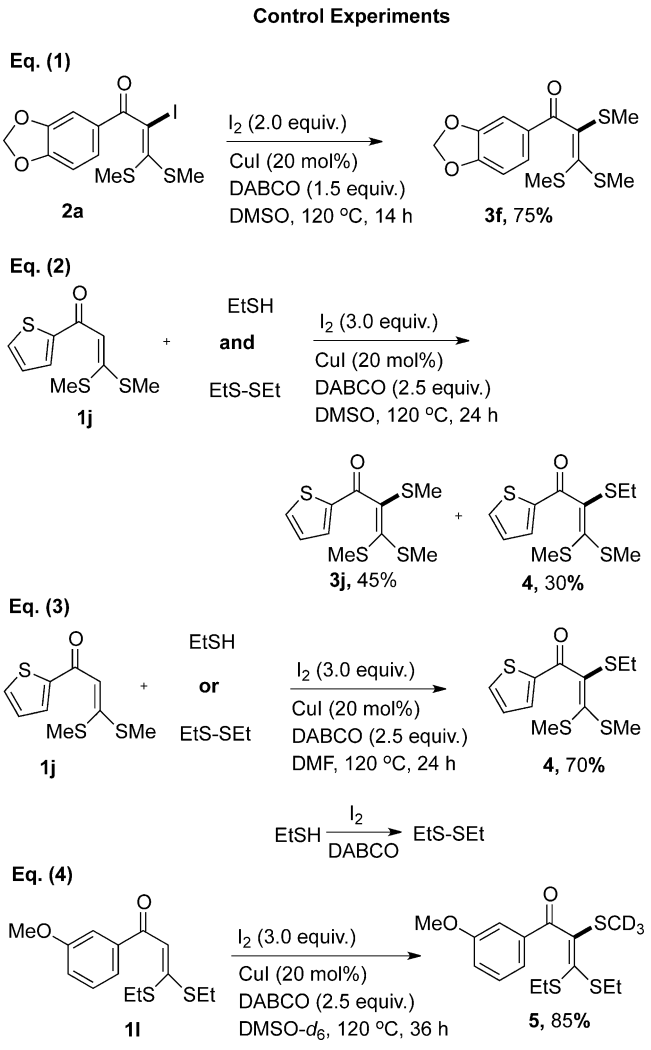


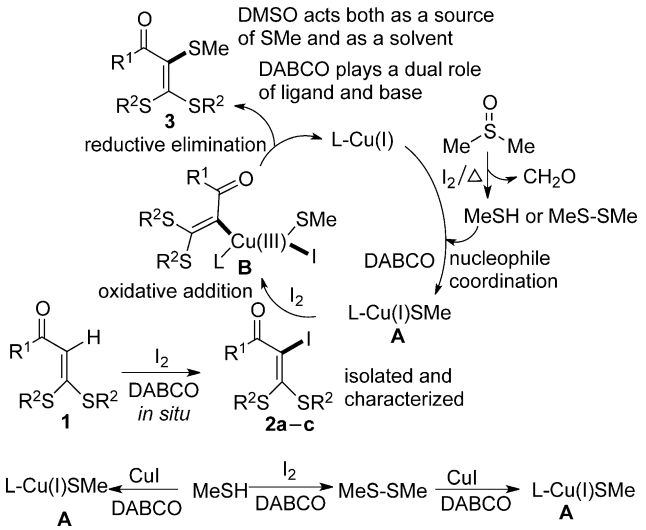
Scheme 3. (Continued)

These reactions provided approximately 70% of thioethylated product **4** [Eq. (3)].

The structure of **4** was fully established by its satisfactory spectral analysis. Thus, the above two sets of reactions clearly suggested the intermediacy of MeSH during the course of the reaction. Furthermore, to confirm the source of the thiomethyl group in this transformation, we treated dithioacetal **1l** with DMSO-d_6 under the optimized conditions. To our great pleasure, dithioacetal **1l** was converted to the corresponding deuterated derivative **5** in 85%. This deuterium labelling experiment confirmed that the source of thiomethyl is DMSO [Eq. (4)].

Based on literature reports and our experimental observations, a plausible reaction scenario is proposed in Scheme 4. First, the α-oxoketene dithioacetal **1** undergoes iodination at the α-position to give α-aroyl-α-iodoketene dithioacetal **2**, which has been isolated and fully characterized. DMSO in the presence of iodine generates precursor MeSH or MeSSMe, which undergoes nucleophilic co-ordination with the Cu(I) species in the presence of DABCO to form complex L-Cu(I)-SMe **A**. Subsequently, complex **A** undergoes oxidative addition with *in situ* formed intermediate **2**





Scheme 4. Possible mechanism for the thiomethylation of DTAs **1** with DMSO.

to form a Cu(III) complex **B** as key intermediate, which upon reductive elimination gave our desired product **3** with elimination of the Cu(I) species to complete the catalytic cycle. Fascinatingly, in the whole reaction sequence, DABCO plays a dual role of ligand as well as base and DMSO acts both as a source of thiomethyl group and as a solvent.

Conclusions

In summary, we have developed a new synthetic strategy for the selective thiomethylation of the α-Csp^2 atom of α-oxoketene dithioacetals by a dimethyl sulfoxide-iodine-Cu(I) system in excellent yield for the first time. The protocol proceeds smoothly employing independent multiple reactions in a one-pot cascade. Owing to the readily available and inexpensive reagents, operationally simple process, broad substrate scope, high functional group tolerance and high yields, this method should expand the scope of activation and thiomethylation of challenging Csp^2–H bonds. Furthermore, the construction of useful motifs utilizing these synthesized molecules as new precursors for other transformations is underway in our laboratory.

Experimental Section

General Remarks

All the commercially available reagents were purchased from Merck, Aldrich, and Fluka, and were used as received. α-Oxoketene dithioacetals were synthesized by reported procedure.[13e] All ^{1}H and ^{13}C NMR spectra were recorded on a JEOL AL 300 FT-NMR spectrometer. Chemical shifts are given as δ values (in parts per million, ppm) with reference to tetramethylsilane (TMS) as the internal standard. The IR spectra were recorded on Perkin–Elmer Spectrum Version 10.03.05 FT-IR spectrophotometer. Mass spectra were recorded on Agilent Q-TOF and Waters-Q-Tof Premier-HAB213 instruments. All the reactions were monitored by TLC using precoated sheets of silica gel G/UV-254 of 0.25 mm thickness (Merck 60F254) using UV light for visualization.

Typical Procedure for the Thiomethylation of α-Oxoketene Dithioacetals (1)

A mixture of α-oxoketene dithioacetal **1** (1.0 mmol), CuI (20 mol%) and DABCO (2.5 equiv.) in 5 mL of DMSO was stirred in presence of 3 equiv. of iodine at 120 °C for the stipulated period of time (see Table 2). After completion of the reaction (monitored by TLC), the mixture was diluted with 10 mL of DCM followed by washing with aqueous $Na_2S_2O_3$ (2×10 mL) and aqueous NH_4Cl (2×10 mL) to remove unutilized iodine and excess of base, respectively. The organic layer was dried over anhydrous Na_2SO_4, and solvent was evaporated under reduced pressure. The crude residue thus obtained was purified by column chromatography over silica gel using increasing percentage of ethyl acetate in hexane as eluent to afford the pure thiomethylated products **3**.

Acknowledgements

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References

[1] a) V. Gomez-Benitez, O. Baldovino-Pentaleon, C. Herrera-Alvarez, R. A. Toscano, D. Morales-Morales, *Tetrahedron Lett.* **2006**, *47*, 5059; b) N. Taniguchi, *J. Org. Chem.* **2004**, *69*, 6904; c) S. M. Soria-Castro, A. B. Penenory, *Beilstein J. Org. Chem.* **2013**, *9*, 467; d) L. C. Schmidt, V. Rey, A. B. Penenory, *Eur. J. Org. Chem.* **2006**, 2210; e) L. Wang, Z.-C. Chen, *Synth. Commun.* **2001**, *31*, 1227.

[2] F.-L. Yang, F.-X. Wang, T.-T. Wang, Y.-J. Wang, S.-K. Tian, *Chem. Commun.* **2014**, *50*, 2111.

[3] a) B. M. Trost, M. Ochiai, P. G. McDougal, *J. Am. Chem. Soc.* **1978**, *100*, 7103; b) B. Movassagh, M. Navidi, *Tetrahedron Lett.* **2008**, *49*, 6712.

[4] a) H. Wang, D. Huang, D. Cheng, L. Li, Y. Shi, *Org. Lett.* **2011**, *13*, 1650; b) H. Guan, H. Wang, D. Huang, Y. Shi, *Tetrahedron* **2012**, *68*, 2728.

[5] C. C. Eichman, J. P. Stambuli, *J. Org. Chem.* **2009**, *74*, 4005.

[6] K. Omura, A. K. Sharma, D. Swern, *J. Org. Chem.* **1976**, *41*, 957.

[7] K. E. Pfitzner, J. G. Moffatt, *J. Am. Chem. Soc.* **1963**, *85*, 3027.

[8] E. J. Corey, M. Chaykovsky, *J. Am. Chem. Soc.* **1962**, *84*, 867.

[9] a) M. B. Floyd, M. T. Du, P. F. Fabio, L. A. Jacob, B. D. Johnson, *J. Org. Chem.* **1985**, *50*, 5022; b) E. Schipper, M. Cinnamon, L. Rascher, Y. H. Chiang, W. Oroshnik, *Tetrahedron Lett.* **1968**, *9*, 6201; c) J. M. McKenna, F. Halley, J. E. Souness, I. M. McLay, S. D. Pickett, A. J. Collis, K. Page, I. Ahmed, *J. Med. Chem.* **2002**, *45*, 2173; d) N. Mupparapu, S. Khan, S. Battula, M. Kushwaha, A. P. Gupta, Q. N. Ahmed, R. A. Vishwakarma, *Org. Lett.* **2014**, *16*, 1152.

[10] a) W. W. Epstein, F. W. Sweat, *Chem. Rev.* **1967**, *67*, 247; b) L. Chu, X. Yue, F.-L. Qing, *Org. Lett.* **2010**, *12*, 1644; c) F.-L. Liu, J.-R. Chen, Y.-Q. Zou, Q. Wei, W.-J. Xiao, *Org. Lett.* **2014**, *16*, 3768; d) S. M. Patil, S. Kulkarni, M. Mascarenhas, R. Sharma, S. M. Roopan, A. Roychowdhury, *Tetrahedron* **2013**, *69*, 8255; e) D. J. Keddie, T. E. Johnson, D. P. Arnold, S. E. Bottle, *Org. Biomol. Chem.* **2005**, *3*, 2593; f) X. Ren, J. Chen, F. Chen, J. Cheng, *Chem. Commun.* **2011**, *47*, 6725; g) Z.

Zhang, Q. Tian, J. Qian, Q. Liu, T. Liu, L. Shi, G. Zhang, *J. Org. Chem.* **2014**, *79*, 8182.
[11] a) X. Gao, X. Pan, J. Gao, H. Huang, G. Yuan, Y. Li, *Chem. Commun.* **2015**, *51*, 210; b) G. Yuan, J. Zheng, X. Gao, X. Li, L. Huang, H. Chen, H. Jiang, *Chem. Commun.* **2012**, *48*, 7513; c) F. Luo, C. Pan, L. Li, F. Chen, J. Cheng, *Chem. Commun.* **2011**, *47*, 5304; d) P. Sharma, S. Rohilla, N. Jain, *J. Org. Chem.* **2015**, *80*, 4116.
[12] a) X. Gao, X. Pan, J. Gao, H. Jiang, G. Yuan, Y. Li, *Org. Lett.* **2015**, *17*, 1038; b) C. Dai, Z. Xu, F. Huang, Z. Yu, Y.-F. Gao, *J. Org. Chem.* **2012**, *77*, 4414.
[13] Recent papers: a) R. K. Verma, H. Ila, M. S. Singh, *Tetrahedron* **2010**, *66*, 7389; b) M. S. Singh, G. C. Nandi, S. Samai, *Green Chem.* **2012**, *14*, 447; c) R. K. Verma, G. K. Verma, G. Shukla, M. S. Singh, *RSC Adv.* **2012**, *2*, 2413; d) G. K. Verma, R. K. Verma, M. S. Singh, *RSC Adv.* **2013**, *3*, 245; e) G. K. Verma, R. K. Verma, G. Shukla, N. Anugula, A. Srivastava, M. S. Singh, *Tetrahedron* **2013**, *69*, 6612.
[14] G. Singh, H. Ila, H. Junjappa, *Synthesis* **1985**, 165.
[15] a) L. Zhu, X. Cao, R. Qiu, T. Iwasaki, V. P. Reddy, X. Xu, S.-F. Yin, N. Kambe, *RSC Adv.* **2015**, *5*, 39358; b) P. J. Amal Joseph, S. Priyadarshini, M. Lakshmi Kantam, B. Sreedhar, *Tetrahedron* **2013**, *69*, 8276.
[16] a) Q. Gao, X. Wu, S. Liu, A. Wu, *Org. Lett.* **2014**, *16*, 1732; b) G. Yin, B. Zhou, X. Meng, A. Wu, Y. Pan, *Org. Lett.* **2006**, *8*, 2245; c) X. Wu, Q. Gao, S. Liu, A. Wu, *Org. Lett.* **2014**, *16*, 2888; d) X. Wu, Q. Gao, M. Lian, S. Liu, A. Wu, *RSC Adv.* **2014**, *4*, 51180.
[17] Note: α-oxoketene dithioacetals with R^1 = Me and R^2 = Bn furnished highly complex TLC patterns with several overlapping spots, which could not be isolated.

