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PII: S0040-4039(14)01614-1
DOI: http://dx.doi.org/10.1016/j.tetlet.2014.09.099
Reference: TETL 45193

To appear in: *Tetrahedron Letters*

Received Date: 8 July 2014
Revised Date: 17 September 2014
Accepted Date: 22 September 2014

Please cite this article as: Gao, Q., Liu, S., Wu, X., Wu, A., Convergent integration of three self-sorting domino sequences: three-component direct synthesis of 3-methylthio-4-aryl-maleimides from methyl ketones with acetonitrile and DMSO, *Tetrahedron Letters* (2014), doi: http://dx.doi.org/10.1016/j.tetlet.2014.09.099

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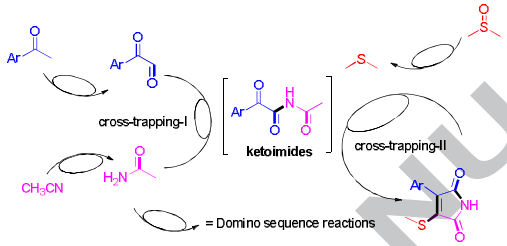

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Convergent integration of three self-sorting domino sequences: three-component direct synthesis of 3-methylthio-4-aryl-maleimides from methyl ketones with acetonitrile and DMSO

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ARTICLE INFO

Article history:
Received
Received in revised form
Accepted
Available online

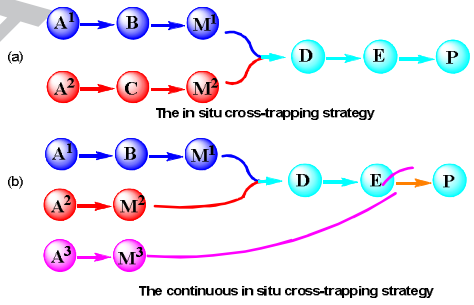
Keywords:
Convergent integration
Self-sorting
Maleimides

ABSTRACT

An I_2-promoted three-component coupling reaction was described for the construction of 3-(methylthio)-4-aryl-1*H*-pyrrole-2,5-diones from methyl ketones with acetonitrile and DMSO. This transformation involved the in situ generation and application of α-ketoimides. Furthermore, DMSO was converted to DMS in situ, which subsequently served as a methylthiolation reagent in the reaction. To the best of our knowledge, this protocol provided the first known example of convergent integration of three self-sorting domino sequences.

1. Introduction

In recently years, many novel and versatile synthetic strategies have been proposed and utilized to generate a diverse range of valuable target molecules.[1] In particular, the in situ trapping of unstable intermediates via linear domino reactions has become a major topic of research interest, due to their high reactivity and ease of transformation to miscellaneous novel structures.[2] Recently, we reported an efficient in situ cross-trapping strategy,[3] and several groups were involved and many synthetically useful transformations have been reported[4] (Scheme 1a). As a continuation of our work, we envisioned that substrates could be simultaneously involved in three different domino sequences, with the in situ trapping of respectively generated intermediates converging on the desired product (Scheme 1b). We report herein an I_2-promoted three-component coulping reaction of methyl ketones with acetonitrile and DMSO to construct 3-(methylthio)-4-aryl-1*H*-pyrrole-2,5-diones via convergent integration of three self-sorting domino sequences.



Scheme 1. In situ trapping strategies.

Thioethers are common functionalities in many biologically active compounds.[5] Among them, methyl aryl sulfides have attracted much attention due to widespread existence in nature.[6] As a consequence, the preparation of aryl methyl thioethers usually involves the reduction of sulfoxides,[7] and the direct or heteroatom-facilitated lithiation of aromatic C–H bonds followed by electrophilic substitution with dimethyl disulfide.[8] Recently, Ma and co-workers reported their successes in methylthiolation procedure using aryl iodines and sulfur by a multistep transformation.[9] Qing[10a] and Cheng[10b] independently described the direct use of DMSO as the reagent for copper-mediated methylthiolation. Very recently, Yu et al. also achieved methylthiolation of heteroarenes with DMSO by using AgF as catalyst and $Cu(OAc)_2$ as mediator/oxidant.[10c] Inspired by our previous work,[11] the methylthiolation using DMSO as the terminal methylthiolation source is described here.

Recently, the construction of α-ketoamides has been developed via oxidative coupling of RH with NH of amines.[12] However, in contrast to NH of amines, the weak nucleophilicity especially free N–H of amides,[13] have not been well investigated. Pleasingly, our research established that methyl ketones could be converted in situ to the corresponding α-ketoaldehydes in the presence of I_2 and DMSO. It was envisaged that the higher reactivity in the aldehyde of 2-oxoaldehyde could facilitate the cross-trapping of an in situ formed acetamide from acetonitrile to afford α-ketoimides. Subsequently, direct α-C_{sp3}–H bonds activation of α-ketoimides could trap DMS generated in situ from DMSO to realize an annulation in one-pot (Scheme 2). This work provided the first known example of metal-free cross-coupling/annulation of methyl ketones with acetonitrile and

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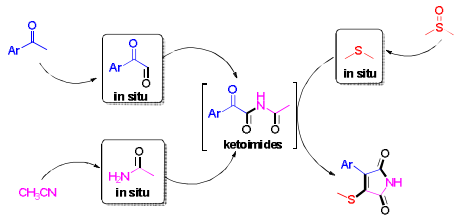
DMSO via α-ketoimides generation and application in situ has been developed.

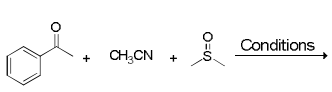


Scheme 2. Design strategy: α-ketoimides generation and application in situ.

2. Results and discussion

The reaction of acetophenone (**1a**) with acetonitrile (**2**) was selected as a model reaction to assess the feasibility of our new strategy. When acetophenone (**1a**) was reacted with acetonitrile (**2**) in the presence of I_2 in DMSO at 100 °C, the direct annulation reaction occurred to afford the expected 3-(methylthio)-4-phenyl-1*H*-pyrrole-2,5-dione (**3a**)[14] in 37% yield. This result was unambiguously confirmed by X-ray crystallography (Supporting Information, Figure S4).[15] Increased amounts of **2a** to 15 equiv provided **3a** in 73% yield (Table 1, entry 4). However, further increases in the amount of I_2 did not provide any additional increases in the yield. And it was determined that the reaction could not occur in the absence of I_2 (Table 1, entry 9), which suggested that I_2 played an important role in the reaction. Generally, the in situ hydration of the nitrile group is performed in the presence of Brønsted acid or base. In this work, the coupling reaction thus used a variety of Brønsted acid and base catalysts. Unfortunately, they were found unable to effectively promote the reaction (Table 1, entries 10–20). Finally, a range of different temperatures were examined for improved yield (Table 1, entries 21–24), and 110 °C was determined as optimal for the cascade reaction.

Table 1. Optimization of the reaction conditions[a]



1a 2 3a

Entry	I_2 (equiv)	Acid	Base	Temp (°C)	Yield (%)[b]
1	1.5	–	–	100	37
2[c]	1.5	–	–	100	42
3[d]	1.5	–	–	100	64
4[e]	1.5	–	–	100	73
5[e]	0.5	–	–	100	< 5
6[e]	1.0	–	–	100	35
7[e]	1.2	–	–	100	64
8[e]	2.0	–	–	100	74
9[e]	–	–	–	100	0
10[e]	1.5	CF_3SO_3H	–	100	56
11[e]	1.5	PTSA	–	100	45
12[e]	1.5	HOAc	–	100	60
13[e]	1.5	CH_3SO_3H	–	100	41
14[e]	1.5	TFA	–	100	42
15[e]	1.5	H_2SO_4	–	100	54
16[e]	1.5	–	DIPEA	100	< 10
17[e]	1.5	–	DBU	100	< 5
18[e]	1.5	–	Et_3N	100	0
19[e]	1.5	–	K_3PO_4	100	0
20[e]	1.5	–	$NaHCO_3$	100	0
21[e]	1.5	–	–	80	0
22[e]	1.5	–	–	90	71
23[e]	**1.5**	**–**	**–**	**110**	**82**
24[e]	1.5	–	–	120	81

[a] Reaction conditions: **1a** (0.5 mmol), **2** (1.5 mmol), acid or base (0.5 mmol), DMSO (2 mL).

[b] Isolated yields.

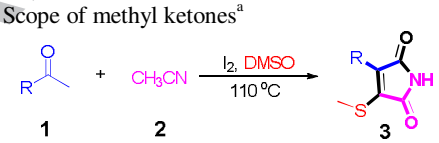
[c] **2** (2.5 mmol).

[d] **2** (5.0 mmol).

[e] **2** (7.5 mmol).

With the optimized conditions in hand, the generality and scope of the molecular iodine-promoted direct synthesis of maleimides was subsequently explored. To our delight, the reaction demonstrated a wide scope for the structure of aromatic ketones (Table 2). Aryl methyl ketones bearing electron-neutral (4-H, 4-Me), electron-rich (4-OMe, 3-OMe, 2-OMe, 3,4-OCH_2O, 3,4-OCH_2CH_2O), and electron- deficient (4-NO_2, 3-NO_2, 4-Ph) groups were directly converted into the corresponding products in moderate to good yields (31–82%; **3a–j**). The electronic and steric nature of the aromatic ketones was shown to influence the reaction efficiency. Much to our satisfaction, the optimized conditions also demonstrated good compatibility with aromatic ketones bearing halogen substituents (4-F, 4-Cl, 4-Br, 3,4-Cl_2), with the corresponding products **3k–n** being obtained in 45–68% yields. Notably, 2-naphthyl methyl ketone and 1-naphthyl methyl ketone also reacted smoothly under the optimized conditions to provide **3o** and **3p** in 72 and 24% yields, respectively. Moreover, the reactions conditions were successfully applied to several heteroaryl ketones, including thienyl, benzofuryl, and indolyl ketones, which provided the desired products in moderate to good yields (59–70%; **3q–s**).

Table 2. Scope of methyl ketones[a]



1 2 3

Entry	**1** (R)	**3**	Yields[b] (%)
1	**1a** (C_6H_5)	**3a**	82
2	**1b** (4-MeC_6H_4)	**3b**	45
3	**1c** (4-$MeOC_6H_4$)	**3c**	76
4	**1d** (3-$MeOC_6H_4$)	**3d**	40
5	**1e** (2-$MeOC_6H_4$)	**3e**	31
6	**1f** (3,4-$OCH_2OC_6H_3$)	**3f**	77
7	**1g** (3,4-$OCH_2CH_2OC_6H_3$)	**3g**	43
8	**1h** (4-$NO_2C_6H_4$)	**3h**	41
9	**1i** (3-$NO_2C_6H_4$)	**3i**	42
10	**1g** (4-PhC_6H_4)	**3j**	65
11	**1k** (4-FC_6H_4)	**3k**	45
12	**1l** (4-ClC_6H_4)	**3l**	62
13	**1m** (4-BrC_6H_4)	**3m**	68
14	**1n** (3,4-$Cl_2C_6H_3$)	**3n**	67
15	**1o** (2-Naphthyl)	**3o**	72
16	**1p** (1-Naphthyl)	**3p**	24
17	**1q** (3-Thienyl)	**3q**	68
18	**1r** (2-Benzofuryl)	**3r**	70
19	**1s** (3-Indolyl)	**3s**	59

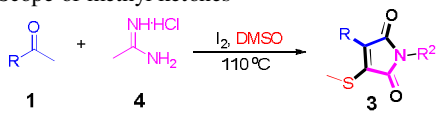
[a] Reaction conditions: **1** (0.5 mmol), **2** (7.5 mmol), and I_2 (0.75 mmol) in DMSO (2 mL) at 110 °C.

[b] Isolated yields.

To improve the practicability of this protocol, acetimidamide hydrochloride was evaluated as a source of acetamide through the procedure. Using 200 mol% acetimidamide hydrochloride, **3a** was obtained in 53% yield accompanying another product 2-oxo-2-phenylacetamide (**5a**) in 38% yield. It was supposed that **5a**

was formed by a hydrolysis reaction in the presence of excessive HCl. Several aryl methyl ketones were subjected to the procedure and the corresponding products were repeatedly obtained in reasonable yields after slight adjustments to the reaction conditions (Table 3).

Table 3. Scope of methyl ketones[a]



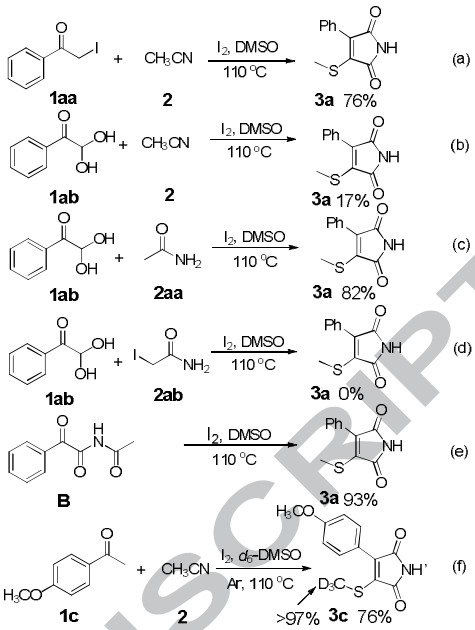
1 4 3

Entry	1 (R)	3	Yields[b] (%)
1	**1a** (C_6H_5)	**3a**	53
2	**1b** (4-MeC_6H_4)	**3b**	55
3	**1c** (4-$MeOC_6H_4$)	**3c**	48
4	**1h** (4-$NO_2C_6H_4$)	**3h**	45
5	**1m** (4-BrC_6H_4)	**3m**	78
6	**1o** (2-Naphthyl)	**3o**	64
7	**1q** (3-Thienyl)	**3q**	57

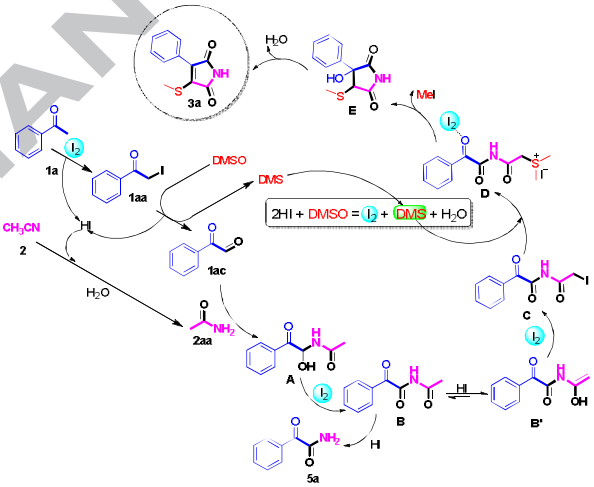
[a] Reaction conditions: **1** (0.5 mmol), **4** (1.0 mmol), and I_2 (0.75 mmol) in DMSO (2 mL) at 110 °C.

[b] Isolated yields.

A series of control experiments were performed to gain some insights into the mechanism. First, α-iodo acetophenone (**1aa**) and hydrated hemiacetal (**1ab**) were subjected to the standard conditions to provide **3a** in 76 and 17% yields, respectively (Scheme 3a and 3b). The reaction of **1ab** with acetamide (**2aa**) was performed under standard conditions to obtain the desired product **3a** in good yield (Scheme 3c). Phenacyl iodine (**1aa**), phenylglyoxal (**1ac**) and acetamide (**2aa**) were thus confirmed as key intermediates in this transformation. However, **3a** was not provided with the application of the standard conditions to 2-iodoacetamide (**2ab**) (Scheme 3d), which indicated that 2-iodoacetamide (**2ab**) was not an intermediate in this reaction process. Furthermore, **B** converted to the desired product **3a** in excellent yields under the standard conditions (Scheme 3e). This indicated that the reaction incorporated the oxidative amidation of acetophenone (**1a**) with acetamide (**2aa**). Finally, DMSO-d_6 examined to explore the potential role of DMSO in the methylthiolation process. DMSO was supported as methylthiolation source by a deuterium labeling experiment (Scheme 3f), where the partially deuterated product **3c-d_3** was generated from DMSO-d_6.



Scheme 3. The controlled experiments.



Scheme 4. The possible mechanism.

Based on our preliminary results and previous works,[16] a possible mechanism was proposed for the iodine-promoted cascade annulation reaction of acetophenone (**1a**) with acetonitrile (**2**) (Scheme 4). Where, substrate **1a** would be converted to α-iodo acetophenone (**1aa**) in the presence of I_2. The subsequent oxidation of **1aa** by DMSO would provide phenylglyoxal (**1ac**). Then, the reaction between the aldehyde group of phenylglyoxal (**1ac**) and the in situ formed acetamide (**2aa**) from the hydrolysis of acetonitrile (**2**) would afford **A**, which would be rapidly oxidized by I_2 to produce α-ketoimide **B**.[17] Subsequent enolization would provide isomer **B'**, which would afford *N*-(2-iodoacetyl)-2-oxo-2-phenylacetamide (**C**) in the presence of I_2.[18] Compound **C** would react with DMS generated in situ from the reduction of DMSO[11] to provide dimethyl(2-oxo-2-(2-oxo-2-phenylacetamido)ethyl)sulfonium iodine (**D**). After the loss of MeI, compound **D** would then undergo an intramolecular aldol-type condensation reaction to produce 3-hydroxy-4-(methylthio)-3-phenylpyrrolidine-2,5-dione (**E**), which would subsequently undertake a dehydration reaction to yield **3a**.

3. Conclusion

In summary, an I_2-promoted three-component cross-coupling/annulation reaction has been described for the construction of 3-(methylthio)-4-aryl-1*H*-pyrrole-2,5-diones from methyl ketones with acetonitrile and DMSO. Initial studies of the mechanism have suggested that this reaction occurred via convergent integration of three self-sorting domino sequences. Notably, the DMS generated in situ from DMSO served as a methylthiolation reagent. More importantly, this metal-free transformation integrated the in situ generation and application of α-ketoimides. Further explorations of this strategy will be reported in due course.

Acknowledgments

We thank the National Natural Science Foundation of China (Grant 21032001 and 21272085). We also thank Dr. Xianggao Meng for his help with X-ray diffraction analysis and Dr. Chuanqi Zhou, Hebei University, for analytical support.

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Supplementary Material

Evidence in support of the hypothetic mechanism, and ^{1}H and ^{13}C NMR spectra and X-ray crystal data for **3a**. Supplementary data related to this article can be found online at doi:

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