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A Highly Tunable Stereoselective Dimerization of Methyl Ketone: Efficient Synthesis of *E*- and *Z*-1,4-Enediones

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ABSTRACT

A new method for the tunable synthesis of 1,4-enedione directly from aromatic methyl ketone is described. This tandem reaction enables the construction of symmetric and unsymmetric 1,4-enediones with complete *E*-selectivity. Moreover, the resulting *E*-1,4-enedione could be transformed into a *Z*-isomer by irradiation with 23 W of white light.

The construction of a carbon−carbon double bond, a principal functionality in organic chemistry, plays a central role in chemical synthesis.[1] Therefore, various olefination methodologies have been developed over the past decades.[2] Among these versatile protocols, direct functionalization of inert C—H bonds, involving coupling reactions of C_{aryl}—H bonds with C_{vinyl}—H bonds[3] and double C_{vinyl}—H bond activation,[4] has emerged as a step-economic and powerful tool for carbon−carbon double bond formation. However, owing to the general low reactivity of C(sp^3)—H bonds, direct functionalization of two sp^3 C—H bonds to generate a C=C bond with high selectivity remains a great challenge.[5]

As an important class of olefins, the 1,4-enedione ($R_1COCH{=}CHCOR_2$) compound has attracted noteworthy attention in recent years since it constitutes a key component of many bioactive compounds including steroids, antitumor agents, and marine natural products.[6]

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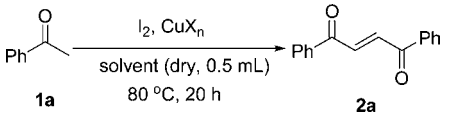
Conventional synthetic routes to 1,4-enedione units involve ring opening of furan and thiophene derivatives,[7] the oxidation of an enone subunit,[8] and decomposition of α-diazo carbonyl compounds.[9] Recently, Kirsch reported a useful oxidative rearrangement of 2-alkynyl alcohols to yield 1,4-enediones in 33−65% yield.[10] Although considerable progress has been made in 1,4-enedione synthesis, the limited availability of starting materials restricts the substitution pattern of the product, and the low yield also limits its synthetic application. In addition to these problems, great challenges remain in the synthesis of symmetric and unsymmetric 1,4-diaryl-substituted 1,4-enedione, and there is no single method providing a universal solution to the stereoselective tunable synthesis. We envisioned that construction of a 1,4-diaryl substituted 1,4-enedione unit directly from aromatic methyl ketone would be a more appreciable synthetic route, since the direct transformation of two simple C(sp^3)—H bonds into the C=C bond eliminates prefunctionalization steps for substrate activation. Herein, we first report an efficient synthesis of symmetric and unsymmetric 1,4-enediones directly from commercially available aromatic methyl ketones in a complete *E*-selective manner. Moreover, the resulting *E*-1,4-enedione could be transformed into a *Z*-isomer by irradiation with white light (23 W) at rt with high to excellent *E*/*Z* photoconversions.

Table 1. Optimization of the Reaction Conditions[a]

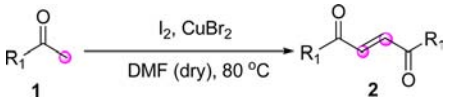


entry	solvent	yield (%)[b]
1[c]	DMF	43
2	DMF	76
3[d]	DMF	0
4[e]	DMF	76
5[f]	DMF	72
6[g]	DMF	31
7[h]	DMF	74
8	DMA	45
9	DMSO	trace
10	CH_3NO_2	trace
11	Tol	trace
12[i]	DMF	77
13[j]	DMF	56

[a] The reactions were carried out in a sealed tube with **1a** (0.5 mmol), I_2 (2 equiv), $CuBr_2$ (0.2 equiv), and solvent (dry, 0.5 mL) at 80 °C for 20 h. [b] Isolated yield. [c] No copper salt was added. [d] No iodine was added. [e] Using 3 equiv of iodine. [f] 1 equiv of water was added. [g] 10 equiv of water were added. [h] The reaction temperature was 90 °C. [i] The reaction was performed under 1 atm of oxygen. [j] The reaction was performed under 1 atm of nitrogen.

With the homodimerization of acetophenone **1a** as a model reaction, a series of reaction conditions were optimized (Table 1). In a continuing effort to develop iodine-mediated tandem reactions,[11] a preliminary study revealed that iodine could promote the homodimerization of acetophenone **1a** to yield the product **2a** in 43% yield (Table 1, entry 1). Then, experiments were performed to investigate the effect of Lewis acids on the reaction, and $CuBr_2$ was identified to be the suitable Lewis acid to give the best chemical yield (see Table S1 in the Supporting Information for details). Further study showed that iodine was essential for this transformation (Table 1, entry 3). Increasing the temperature to 90 °C led to a slight decrease in the yield (Table 1, entry 7). Subsequently, different polar and nonpolar solvents were examined (Table 1, entries 8−11), and the results revealed the superiority of *N*,*N*-dimethylformamide (DMF) as solvent with respect to the chemical yield (Table 1, entry 2 vs entries 8−11). Further assessment of the reaction conditions indicated that an oxygen atmosphere had little effect on the reaction activity; however, a nitrogen atmosphere would lead to a decrease in the chemical yield (Table 1, entries 12 and 13).

Table 2. Scope of the Homodimerization Reaction[a]



entry	R^1	product	yield (%)[b]
1	C_6H_5	**2a**	77
2	4-MeC_6H_4	**2b**	78
3	4-*t*-BuC_6H_4	**2c**	82
4	4-*n*-BuC_6H_4	**2d**	90
5	4-*i*-BuC_6H_4	**2e**	89
6	4-$MeOC_6H_4$	**2f**	91
7	4-FC_6H_4	**2g**	75
8	4-ClC_6H_4	**2h**	70
9	4-$CF_3C_6H_4$	**2i**	29
10	3-MeC_6H_4	**2j**	72
11	3-$MeOC_6H_4$	**2k**	74
12	3-FC_6H_4	**2l**	68
13	2-MeC_6H_4	**2m**	65
14	2-FC_6H_4	**2n**	61
15	2,5-di-$MeOC_6H_3$	**2o**	83
16	2-thio	**2p**	61

[a] The reactions were carried out with **1a** (0.5 mmol), I_2 (2 equiv), $CuBr_2$ (0.2 equiv), and DMF (dry, 0.5 mL) at 80 °C for 20 h. [b] Isolated yield.

With the optimized reaction conditions in hand, the substrate scope and limitations of the homodimerization reaction were investigated by evaluating a variety of aromatic methyl ketones. As illustrated in Table 2, the reaction proceeded smoothly with different substrates to afford a wide range of 1,4-diaryl-substituted 1,4-enediones in complete *E*-selectivity. The electronic properties of a series of aromatic methyl ketones were found to greatly influence

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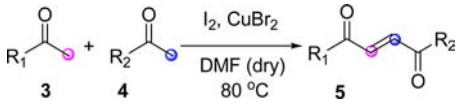
the reaction (Table 2, entries 1−9). In general, the electron-donating group has a positive effect on the yield (Table 2, entries 1−6 vs 7−9). On the other hand, the steric effects of substituents on the aromatic rings also had some influence on the reaction. A heteroaryl substrate was also efficiently transformed, affording the product **2p** in moderate yield (Table 2, entry 15). The absolute configuration of **2a** was determined by single-crystal X-ray diffraction analysis (CCDC 918566).

As shown in Table 2, the homodimerization of aromatic methyl ketone has been demonstrated as a step-economic method for symmetric 1,4-enedione synthesis. It would be more valuable if the present reaction system could be applied to unsymmetric 1,4-diaryl substituted 1,4-enedione synthesis, since an unsymmetric 1,4-enedione moiety is an important structural feature found in many biologically relevant compounds.[12] However, the rapid and stereoselective synthesis of these units remain an ongoing synthetic challenge. It was found that a minor modification of the standard reaction conditions led to the formation of heterodimerized products **5a**−**5l** in synthetically useful yields, in which a 2-fold excess of one ketone over the other was employed to facilitate heterodimerization. As presented in Table 3, both electron-withdrawing and -donating functionalities on the aromatic ring of methyl ketones were compatible with this heterodimerization reaction, yielding **5a**−**5l** in 58−83% yields.

Table 3. Scope of the Heterodimerization Reaction[a]

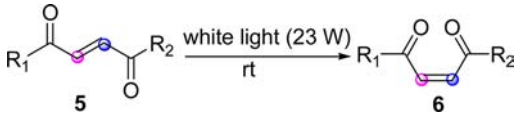


entry	R_1	R_2	product	yield (%)[b]
1	C_6H_5	4-$MeOC_6H_4$	**5a**	83
2	4-MeC_6H_4	4-$MeOC_6H_4$	**5b**	65
3	3-MeC_6H_4	4-$MeOC_6H_4$	**5c**	62
4	2-MeC_6H_4	4-$MeOC_6H_4$	**5d**	58
5	4-FC_6H_4	4-$MeOC_6H_4$	**5e**	72
6	3-FC_6H_4	4-$MeOC_6H_4$	**5f**	65
7	2-FC_6H_4	4-$MeOC_6H_4$	**5g**	61
8	4-*n*-BuC_6H_4	4-$MeOC_6H_4$	**5h**	74
9	4-*i*-BuC_6H_4	4-$MeOC_6H_4$	**5i**	70
10	C_6H_5	4-*n*-BuC_6H_4	**5j**	58
11	4-FC_6H_4	4-*n*-BuC_6H_4	**5k**	70
12	4-FC_6H_4	2-thio	**5l**	63

[a] The reactions were carried out with **3** (0.5 mmol), **4** (0.25 mmol), I_2 (2 equiv), $CuBr_2$ (0.2 equiv), and DMF (dry, 0.5 mL) at 80 °C for 20 h. [b] Isolated yield.

As shown above, the symmetric and unsymmetric 1,4-enediones can be synthesized in complete *E*-selectivity under the $I_2/CuBr_2$ reaction system. We wondered whether the *E*-1,4- enedione could be transformed into the *Z*-isomer with a rapid and practical protocol. Careful inspection of the literature describing *E*/*Z* isomerization of 1,4-enedione reveals that high pressure mercury (200 W) and degassed Et_2O are needed.[13] Herein, we described a photoisomerization of *E*-1,4-enedione into the *Z*-isomer by irradiation with white light (23 W) at rt. As illustrated in Table 4, a series of symmetric and unsymmetric *E*-1,4-enediones with different substituents on the aromatic ring underwent the photoisomerization smoothly, yielding *Z*-1,4-enediones **6a**−**6i** with high to excellent *E*/*Z* photoconversions. The absolute configuration of **6a** was determined by single-crystal X-ray diffraction analysis (CCDC 918565). Compared to the previously reported method, the present protocol may be more appealing for laboratory applications due to its operational simplicity.[14]

Table 4. Scope of the Photoisomerization Reaction[a]



entry	R_1	R_2	product	yield (%)[b]
1	C_6H_5	C_6H_5	**6a**	99
2	4-MeC_6H_4	4-MeC_6H_4	**6b**	93
3	4-*i*-BuC_6H_4	4-*i*-BuC_6H_4	**6c**	97
4	4-$MeOC_6H_4$	4-$MeOC_6H_4$	**6d**	81
5	3-$MeOC_6H_4$	3-$MeOC_6H_4$	**6e**	88
6	3-FC_6H_4	3-FC_6H_4	**6f**	87
7	C_6H_5	4-$MeOC_6H_4$	**6g**	90
8	4-*n*-BuC_6H_4	4-$MeOC_6H_4$	**6h**	89
9	4-FC_6H_4	4-$MeOC_6H_4$	**6i**	81

[a] The reactions were carried out with **5** (0.3 mmol), solvent (2.1 mL, EtOAc/Hex = 1:6) by irradiation with 23 W of white light at rt for 5 h. [b] Isolated yield.

To gain insight into the mechanism of this dimerization reaction, a series of control experiments were set up (see eqs 1−3 in the Supporting Information for details). The control

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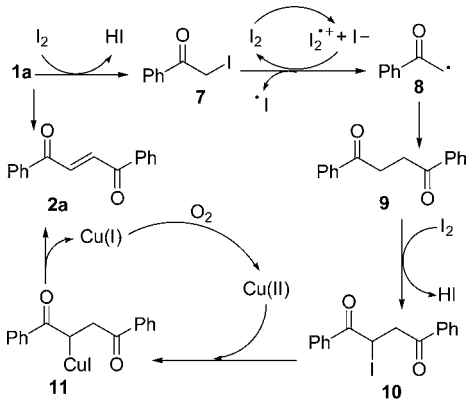
Scheme 1. Possible Mechanism for the Formation of **2a**



experiments show that this tandem reaction involves a radical process and compounds **7** and **9** are key intermediates of this reaction. On the basis of the control experiments and previous studies,[15] a possible pathway of the present dimerization reaction was shown in Scheme 1. Initially, iodination of acetophenone **1a** yields phenacyl iodine **7**, accompanied by the liberation of one molecule of HI. Then, phenacyl radical **8** is generated from α-iodo ketone **7** with the participation of iodine. Subsequent radical coupling leads to the formation of 1,4-dione **9**.[16] Iodination of dibenzoylethane **9** affords compound **10**, accompanied by the generation of another molecule of HI. Then, copper(II) is inserted into the C−I bond to yield intermediate **11**, which subsequently undergoes a β-H elimination to yield corresponding product **2a** with complete *E*-selectivity. Molecular iodine plays two important roles in the tandem reaction: iodination and induction of the phenacyl radical **8** formation. However, the molecular iodine can be recovered after inducing the phenacyl radical formation; therefore, only 2 equiv of iodine compared to acetophenone **1a** are needed in the dimerization reaction. The high selectivity in the heterodimerization reaction could be explained by the persistent-radical effect (PRE).[17] Since the reaction is not a radical chain reaction, the concentration of the radicals in the mixture should be high enough to obtain efficient radical/radical coupling. The excess of one ketone compared to the other will lead to an increase of the relative concentration of one phenacyl radical with respect to the other, and hence the concentration difference would then be the reason for the selective cross-coupling.

In conclusion, a new and facile method for the tunable synthesis of 1,4-enedione directly from aromatic methyl ketone was described. The present tandem reaction enables the construction of symmetric and unsymmetric 1,4-enedione with complete *E*-selectivity. Moreover, the resulting *E*-1,4-enedione could be transformed into a *Z*-isomer by irradiation with 23 W of white light with good to excellent photoconversions. Further studies to clearly understand the mechanism are ongoing in our laboratory.

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Supporting Information Available. Detailed experimental procedures and spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.

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