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A three-component iodine-catalyzed oxidative coupling reaction: a heterodifunctionalization of 3-methylindoles†

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A metal-free method for the synthesis of heterodifunctional indole derivatives is developed through TBHP/KI-mediated oxidative coupling. The reaction constructs C–O and C–C bonds in succession with the help of *tert*-butyl peroxy radicals generated by the TBHP/KI catalytic system, enabling the direct realization of the heterodifunctionalization of indole in one pot. The product of this reaction is a novel heterodifunctional compound. This work might provide a new effective method for the synthesis of polycyclic indole compounds.

Introduction

Indole is an important structural component which widely exists in natural products and biological metabolites.[1] It is also employed generally in pharmaceuticals, pesticides, and materials.[2] Because of this reason, the efficient synthesis and functionalization of indole derivatives have attracted more and more attention. Over the past decade, many chemical researchers who were interested in the functionalization of indole had proposed a variety of synthesis methods for the functionalization of indole *via* direct C–H bond functionalization and/or C–C bond construction approaches, but most of them only focused on the functionalization of C2/C3 in indole.[3] A few of them could achieve the multi-substitution functionalization of both C2 and C3 in indole,[4] especially for heterodifunctionality.[5]

Peroxide is a key pharmacophore due to its important role in fighting a variety of diseases,[6] such as cancer,[7] HIV[8] and malaria.[9] Peroxy bonds (–O–O–) are widely found in organic compounds, and can be converted to a hydroxyl group under reductive conditions.[10] On the other hand, the 3-hydroxyoxindole moiety has been introduced as an active unit in biological molecules (Fig. 1a),[11] and the indole derivative bearing an ester group at the C2-position is known as an effective drug intermediate (Fig. 1b).[12] The functionalization of indole at the C2- and C3-positions has been reported with the introduction of ester and peroxide groups, respectively,[13,14] but the heterodifunctionalization of indole with both ester and peroxide groups has not been found. It would be a piece of interesting work to explore a new reaction system for the synthesis of difunctional indoles, consistent with the development of indole chemistry and its related functional pharmacological chemistry.

Pihko and his co-workers developed a three-component oxidative functionalization of indole[15] with the use of palladium compounds as catalysts (Scheme 1a). Highly active azo compounds have been used as substrates in the construction of sulfone compounds in oxidative catalytic or photocatalytic systems[16,4b] (Scheme 1b). Carbonyl and sulfone groups have been introduced to indole in the presence of an oxidant or a reductant[17] (Scheme 1c). The difunctionalization of indole can also be achieved under acid catalysis using phosphate esters and carbonyl compounds as starting materials[18] (Scheme 1d). Despite all these achievements, the heterodifunctionalization of indole in one-pot remains an attractive approach from the perspective of step economy and chemical specificity. Motivated by these considerations, we report here a simple and efficient method for the synthesis of heterodifunctionalized indoles using TBHP and potassium iodide as a catalytic

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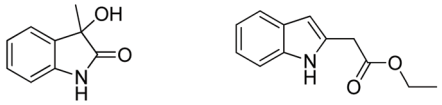
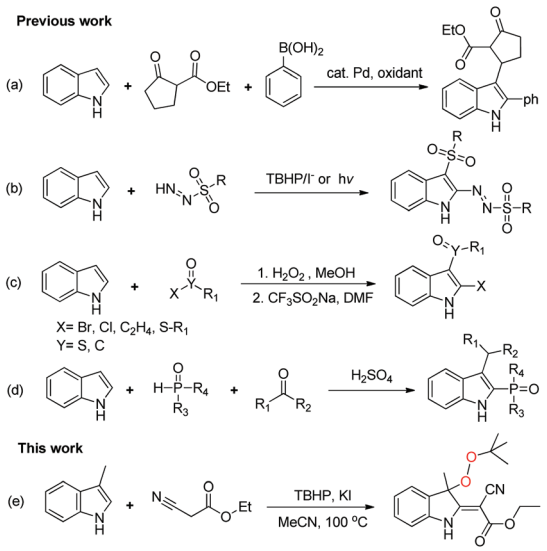


(a) 3-hydroxy-3-methyloxindole (b) ethyl indole-2-acetate

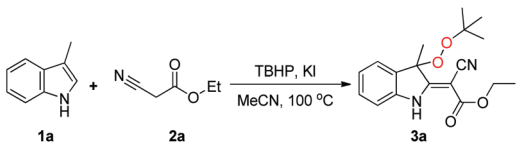
Fig. 1 Representative applications.



Scheme 1 Methods for the preparation of functionalized indole.

system, from which the ester group and peroxy group were added to 3-methylindole at the C2- and C3-positions, respectively (Scheme 1e).

Table 1 Optimization of the reaction conditions[a]



Entry	Catalyst	TBHP[b]	Solvent	Temperature, °C	Yield[d], %
1	**KI**	**5 equiv.**	**MeCN**	**100**	**86**
2	**TBAI**[c]	5 equiv.	MeCN	100	57
3	**NaI**	5 equiv.	MeCN	100	34
4	**NIS**	5 equiv.	MeCN	100	15
5	**I_2**	5 equiv.	MeCN	100	0
6	**None**	5 equiv.	MeCN	100	0
7	KI	**3 equiv.**	MeCN	100	12
8	KI	**7 equiv.**	MeCN	100	84
9	KI	5 equiv.	**THF**	100	66
10	KI	5 equiv.	**1,4-Dioxane**	100	74
11	KI	5 equiv.	**Toluene**	100	35
12	KI	5 equiv.	MeCN	**120**	72
13	KI	5 equiv.	MeCN	**80**	68
14	KI	5 equiv.	MeCN	**60**	59

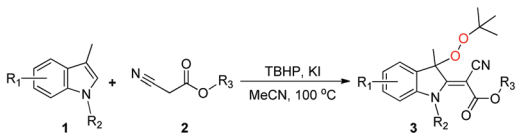
[a] Reaction conditions: **1a** (0.2 mmol), **2a** (1.0 mmol), TBHP, catalyst (0.02 mmol), solvent (0.5 mL), N_2, temperature, 12 h. [b] TBHP = *tert*-butyl hydroperoxide. [c] TBAI = tetra-*n*-butylammonium iodide. [d] Yields were determined by ^{1}H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as the internal standard.

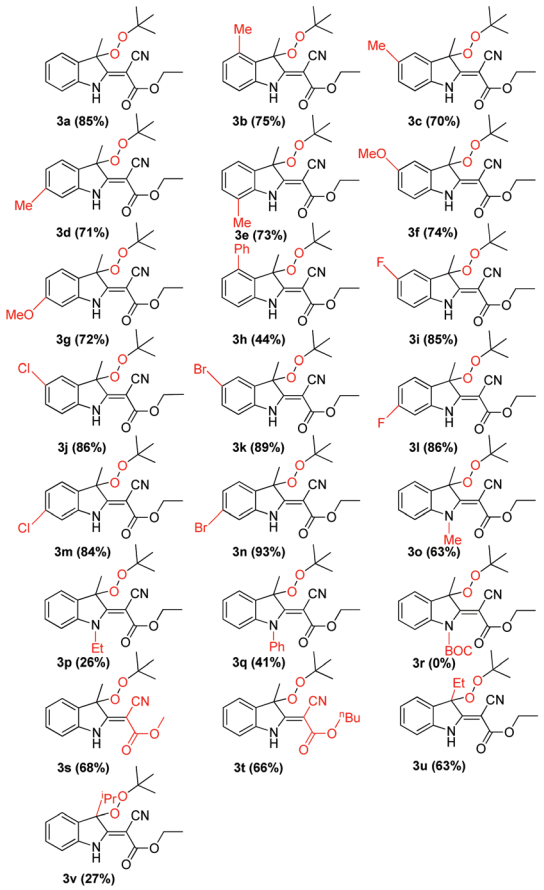
Results and discussion

We commenced the study by choosing 3-methylindole (**1a**) and ethyl cyanoacetate (**2a**) as model substrates to find out the most suitable conditions (Table 1). The results showed that the combination of substrates **1a** and **2a** (1 : 5), KI as the catalyst (10 mol%), and TBHP (TBHP = *tert*-butyl hydroperoxide, 5 equiv.) as the oxidizing agent in acetonitrile under a N_2 atmosphere at 100 °C provided the best results, affording the product **3a** in 86% yield based on 3-methylindole (entry 1). Other iodide sources such as TBAI (TBAI = tetra-*n*-butylammonium iodide), NaI, NIS (NIS = *N*-iodosuccinimide) and iodine afforded the product in lower yields or without yield (entries 2–5). The reaction without the addition of KI did not give the target compound as well (entry 6). A lower amount of TBHP would decrease the yield dramatically down to 12% (entry 7), but a larger amount of TBHP (7 equiv.) would not bring about additional yield (entry 8). The type of solvent was important for the formation of **3a** (entries 6–11). The reaction proceeded smoothly in MeCN (entry 1). Less polar solvents such as THF, 1,4-dioxane, and toluene were unfavorable for the generation of the product with the decline of yield to 35% in toluene (entries 9–11). Higher temperature (120 °C) would cause a slight decrease in the yield of **3a** (entry 12), and lower temperature (<100 °C) was of no advantage to the reaction (entries 13 and 14).

With the optimal reaction conditions in hand, we sought to investigate the generality and functional group compatibility of this transformation under the established conditions (Table 2). The results are presented in Table 2 (**3a–3n**). When the substituent group on the indole-benzene ring was an electron-donating group (EDG), such as methyl and methoxy groups, the products were obtained in similar yields (**3b–3g**, 70–75%). This showed that the EDG had little effect on the production of compounds. The phenyl group had a larger spatial structure, and the steric effect was not conducive to the attack of the *tert*-butyl peroxide group on C3 of 3-methylindole. Thus, the reaction of 3-methyl-4-phenyl-1*H*-indole afforded the compound **3h** in a yield of only 44%. The presence of phenyl groups was likely to hinder the formation of **3h**. Halogen-containing indoles could bring about the desired products in excellent yields under the same reaction conditions (**3j–3n**). The effect of the substituents on the indole nitrogen was also studied. The results showed that the stronger the electron-donating ability of the electron-donating group (*e.g.*, methyl and ethyl), the worse the production efficiency (**3o** and **3p**). The phenyl group substituted indole on the nitrogen atom provided the product in much lower yield (**3q**, 41%), and the reaction of indole substituted with the strong electron-withdrawing group *tert*-butyloxycarbonyl (BOC) showed nonexistence of the product completely (**3r**). Moreover, the reaction of the methyl and butyl substituted cyanoacetate produced the target compounds **3s** (Fig. S1†) and **3t** in 68% and 66% yields, respectively. In addition, we changed the methyl substituent at the C3-position to ethyl (**3u**), isopropyl (**3v**), and butyl groups. The results showed that the yields of the reactions decreased with the increase of the steric hindrance of the substituent at the C3-position (**3u** and **3v**). No target compound was found in the reaction of the butyl-group-substituted indole in our system.

Table 2 Reaction scope with various 3-methylindole derivatives[a,b]





[a] Reaction conditions: **1a** (0.2 mmol), **2a** (1.0 mmol), TBHP (1.0 mmol, 5 M in decane), KI (0.02 mmol), MeCN (0.5 mL), N_2, 100 °C, 12 h. [b] Isolated yields.

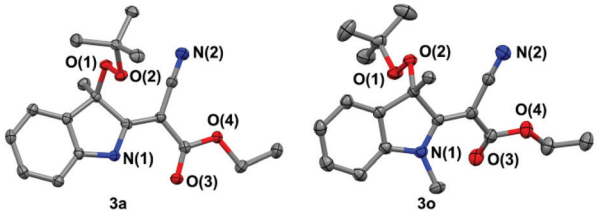
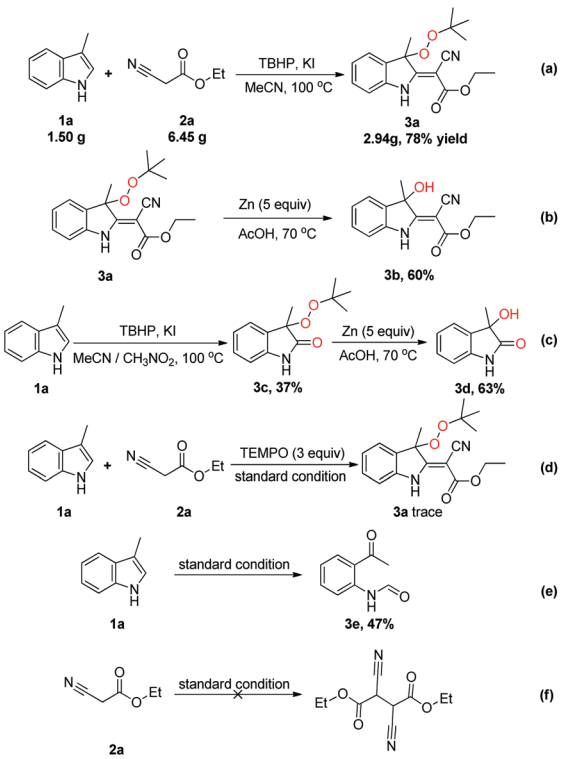


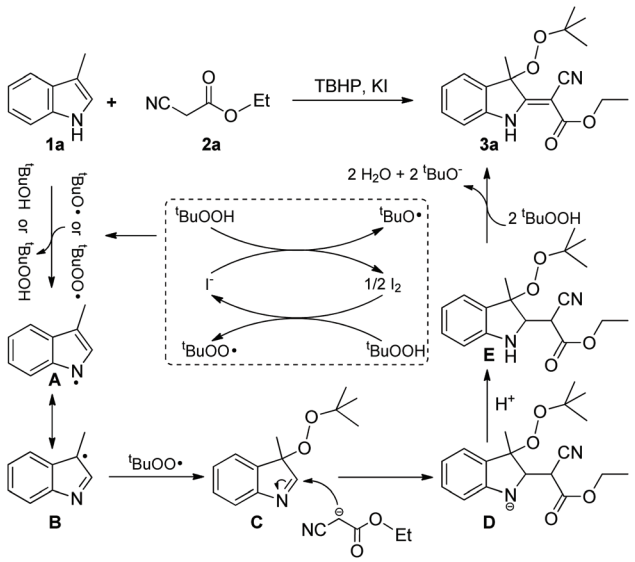
Fig. 2 Crystal structures of compounds **3a** (CCDC: 2064845†) and **3o** (CCDC: 2067966†).



Scheme 2 Control experiments.

The crystal structures of compounds **3a** and **3o** were determined by X-ray crystallography (Fig. 2). In addition, the synthetic utility of our reaction was examined by performing the experiments on gram scale. The reaction of 3-methylindole (**1a**) and ethyl cyanoacetate (**2a**) on a 1.5 gram scale under the standard conditions generated the compound **3a** in 78% yield (Scheme 2a). Furthermore, the target compound **3a** could be reduced to compound **3b** by zinc powder under acidic conditions in 60% yield (Scheme 2b). This type of transformation was supported by the reaction shown in Scheme 2c, where the oxidation of 3-methylindole by TBHP/KI in a mixed solvent of MeCN/$MeNO_2$ provided the compound **3c**, and the reduction of **3c** by zinc powder under acidic conditions afforded the compound **3d** in 63% yield. The compound **3d** has been reported as an active unit in biological molecules (Fig. 1a).

In order to study the reaction mechanism, a couple of experiments were carried out accordingly (Scheme 2d–f). The reaction of the formation of compound **3a** was repeated with the addition of TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) as a radical scavenger under the standard conditions (Scheme 2d). The yield of the reaction decreased to a trace amount (<1%) from 86% in the presence of TEMPO, which indicated the generation of radicals in the process of the reaction. Interestingly, the reaction of 3-methylindole (**1a**) without the presence of ethyl cyanoacetate (**2a**) under the standard conditions afforded the unexpected product **3e** (Scheme 2e), which was supposed to be formed in relation to the generation of the indolyl radical as reported in the literature.[19] Meanwhile, the reaction of ethyl cyanoacetate (**2a**) without the presence of 3-methylindole (**1a**) under the same conditions did not generate any new species with the recovery of starting material **2a** completely (Scheme 2f).



Scheme 3 Possible reaction mechanism.

On the basis of the above results, a possible mechanism is proposed in Scheme 3. The stirring of TBHP and KI in MeCN formed a TBHP/I^- catalytic system, from which *tert*-butoxyl and *tert*-butyl peroxy radicals were generated.[20] The free radicals reacted with 3-methylindole (**1a**) to produce the intermediate **A**, which turned into intermediate **B** *via* an intermolecular electron transfer. The reaction of **B** and the *tert*-butyl peroxy radical led to the formation of intermediate **C**. The carbon atom of the C═N group of **C** was attacked by the ethyl cyanoacetate anion to form the intermediate **D**. The protonation of **D** formed the intermediate **E**, which was oxidized by two equivalents of TBHP to give the final product **3a**.

Conclusions

In summary, we have developed an efficient method for the synthesis of heterodifunctional indole in the TBHP/KI catalytic system. Compared to previous work, this strategy is superior in achieving the heterodifunctionalization of indole molecules with the introduction of both the ester group and *tert*-butyl peroxy group to the indole ring. Our work might provide a way to synthesize multi-substituted indole derivatives for further organic synthesis.

Experimental section

Indole derivative **1a** (0.20 mmol), ethyl cyanoacetate **2a** (1.00 mmol), potassium iodide (0.02 mmol), TBHP (1.0 mmol) and MeCN (0.5 mL) were mixed in a 50 mL Teflon screw-cap sealed tube. The tube was charged with N_2, and the solution was vigorously stirred at 100 °C for 12 h. After cooling to room temperature, the reaction mixture was diluted with dichloromethane (5 mL), and then concentrated under reduced pressure. The crude product was purified on a silica gel column eluted with petroleum ether/acetone (4 : 1 v/v) to afford the target products in yields up to 93% (**3n**). Detailed experimental processes are given in the ESI.†

Conflicts of interest

There are no conflicts to declare.

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