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NaI-mediated Divergent Synthesis of Isatins and Isoindigoes: A New Protocol Enabled by Oxidation Relay Strategy

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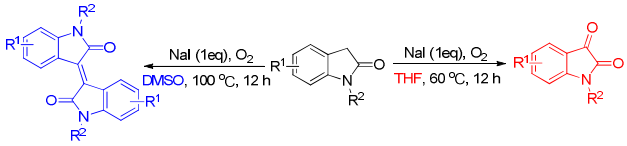
A new approach for the synthesis of isatins and isoindigoes by an inexpensive and environmental-friendly NaI-mediated transforma-tion is disclosed. The selectivity could be switched by simply varying the solvent, isatins (using THF) and isoindigoes (using DMSO) could be obtained in moderate to excellent yields.

Oxidation reaction is a widespread and significant strategy in organic synthesis. Traditional methods of oxidation usually involve the direct use of oxidants, which might cause over oxidation issue. "Oxidation Relay Chemistry", as a new oxidation model[1] was developed by our group recently. This strategy can effectively suppress the over-oxidation of the substrate due to the in-situ generation of a small number of halogens (X_2) which serve as oxidant in this transformation. On the other hand, it uses inexpensive and innocuous sodium-iodide (NaI) as catalyst, and air as oxidant. Based on this concept, we thus have developed several examples for the construction of N-S and C-S bonds[2]. To further demonstrate the universality of this strategy, we carried out the synthesis of the isatins (Indoline-2,3-diones) and isoindigoes (1H,1'H-bis(indolyl-3-indeno)-2,2'-diones) from readily available indole-2-ones.

Isatins are ubiquitous and can be found in a range of biologically active natural products[3], synthetic intermediates[4], and pharmaceuticals chemistry[5]. Currently, a number of protocols for the construction of isatins have been reported[6]: 1) strong acid or base-mediated condensation of aniline with chloral hydrate, oxalyl chloride, and diethyl ketomalonate[7]; 2) oxidation of indoles and indoline-2-ones[8, 9]; 3) intramolecular oxidative cyclization using pre-existing ortho-substituents[10]; 4) metal-catalyzed double carbonylation of 2-haloaniline[11]; 5) ring contraction of 3-diazoquinoline-2-4-diones[12]; 6) C-H activation chemistry[13]. However, these processes have limitations with respect to selectivity, scope, yield, and functional group compatibility.

Isoindigoes, as dipolymer of the indoline-2-ones, are important bis-indole heterocyclic molecules and demonstrate special biological activities[14]. For example, Meisoindigo has been subjected to clinical trials and is used as an indirubin substitute in China for the treatment of chronic myelocytic leukemia (CML)[15]. Moreover, isoindigoes can be used to synthesize organic solar cells such as DAD[16], and used in the design of low-band gap semiconductor materials[17]. To date, several strategies for the preparation of isoindigoes were developed such as the homocoupling of isatins and indolin-2-ones[18], metal-catalyzed intramolecular cyclization[19], and polymerization of 3-bromooxindoles[20] or diazooxindoles[21]. However, these protocols suffer from using metal-catalyst, having limited diversity, and harsh reaction conditions. Therefore, how to address issues in the isatins and isoindigoes syntheses becomes a synthetically important question. Herein we describe an intriguing method using NaI as an efficient mediator to prepare the targeted isatins and isoindigoes. This protocol is highlighted by its simple operation, metal-free conditions, and highly functional group compatibility as shown in Scheme 1.



Scheme 1. Divergent synthesis of isatins and isoindigoes.

At the beginning of our investigation, the optimization of reaction conditions was carried out by evaluating a variety of reaction parameters, which uses 1-methylindolin-2-one (**1a**) as a model substrate (Table 1). Inspired by our previous work[2], we firstly tested the reaction of **1a** in the presence of 1.0 equivalent of NaI in dimethylformamide (DMF) at 100 °C. After 12 h, the desired products **2a** and **3a** were obtained in 33% and 15% yield (Table 1, entry 1), respectively. At that point, a

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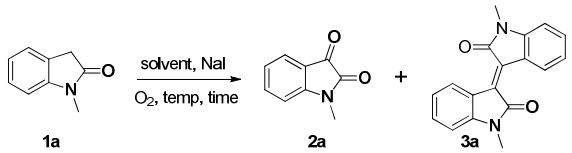
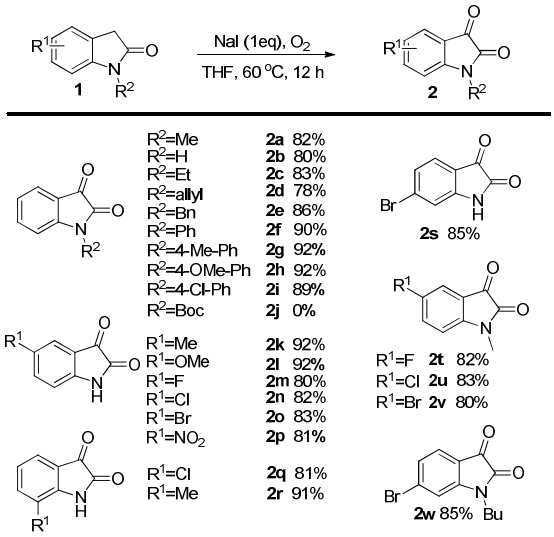
series of solvents were tested (Table 1, entries 2-7). To our delight, **2a** was obtained in 82% yield when THF was used (Table 1, entry 4). The results of control-reactions in the absence of O_2 or NaI (Table 1, entries 8-9) indicated that both O_2 and NaI played a vital role in this transformation. Increasing or decreasing the quantity of NaI gave lower yields of **2a** (Table 1, entries 10-11). The effect of temperature was also examined for **2a**, and 60 °C was found to be the best of choice (Table 1, entries 4 and 12). To our surprise, **3a** could be obtained in 68% yield while DMSO was used as solvent instead of THF (Table 1, entry7). Changing temperature or the quantity of NaI showed a negative influence, delivering **3a** in inferior yields (Table 1, entries 13-16). Subsequently, we tried to increase the yield of **3a** by prolonging the reaction time, and only little improvement was observed. (Table 1, entries 17-18).



Entry	Solvent	Temp. (°C)	Yield [2a] (%)	Yield [3a] (%)
1	DMF	100	33	15
2	Toluene	100	N.R.	N.R.
3	*n*-PrCN	100	38	10
4	THF	60	82	15
5	Dioxane	100	5	<1
6	NMP	100	<5	<1
7	DMSO	100	29	68
8[b]	THF	60	0	0
9[c]	THF	60	0	0
10[d]	THF	60	38	20
11[e]	THF	60	67	24
12	THF	40	43	9
13[d]	DMSO	100	15	25
14[e]	DMSO	100	19	50
15	DMSO	80	25	55
16	DMSO	120	27	66
17[f]	DMSO	100	22	69
18[g]	DMSO	100	20	70

Table 1: Optimization of the reaction conditions [a]. [a] Reaction conditions: **1a** (0.1 mmol), NaI (0.1 mmol), O_2 (1 atm), and solvent (1 mL) for 12 h. Isolated yields. [b] The reaction was conducted under Ar atmosphere. [c] The absence of NaI. [d] NaI was used in 0.05 mmol (0.5 eq). [e] NaI was used in 0.2 mmol (2.0 eq). [f] The reaction time was 16 h. [g] The reaction time was 20 h. *n*-PrCN = Butanenitrile.

Encouraged by the optimized conditions, we then explored the generality of this newly developed protocol. A variety of different oxindoles were converted into the corresponding isatins in excellent yields (Scheme 2). Substrates bearing hydrogen (**2b**), ethyl (**2c**), allyl (**2d**), benzyl (**2e**), phenyl (**2f**), p-tolyl (**2g**), 4-methoxyphenyl (**2h**), and 4-chlorophenyl (**2i**) groups on nitrogen atom illustrated better reactivity in this reaction comparing with the substrate with *tert*-Butyloxy carbonyl (Boc) group (**2j**). Instead, detert-Butyloxy carbonyl product (**2b**) was generated as the major product in 85% yield. Both electron-donating group (**2k, 2l, 2r**) and electron-withdrawing group (**2m-2q, 2s**) on phenyl ring worked well, and the corresponding products were obtained in moderate to excellent yields (80%-92%). In general, the compounds with electron-donating group on phenyl ring could be generated in better yields as compared to the ones with electron-withdrawing group. To further demonstrate the versatility of this protocol, reactions with indolin-2-ones bearing substituents on the phenyl ring and nitrogen atom were then examined (**2t-2w**). The reactions of **1t-1v** bearing a halogen on the phenyl ring and a methyl group on the nitrogen atom provided the expected products **2t-2v** in 82%, 83%, and 80% yields respectively. With **1w** bearing a bromine (Br) on the phenyl and a butyl group on the nitrogen atom produced **2w** in 85% yield. These reactions provide a rapid synthetic route for the synthesis of various isatin derivatives.



Scheme 2. Scope of the oxidation of indolin-2-ones to isatins [a]. [a] Reaction conditions: **1** (0.1 mmol), NaI (0.1 mmol), O_2 (1 atm), 60 °C, THF (1 mL), 12 h.

Next, we focused our attention on isoindigoes. The reactions of a series of substituted indolin-2-ones were examined under the optimal reaction condition (Table 1, entry 7), and the results were summarized in Scheme 3. Substrates bearing hydrogen (**3b**), ethyl (**3c**), phenyl (**3d**), benzyl (**3e**), p-tolyl (**3f**), 4-methoxyphenyl (**3g**), and 4-chlorophenyl (**3h**) groups on nitrogen atom displayed better reactivity in this reaction, and produced isoindigoes efficiently. However, the substrate with *tert*-Butyloxy carbonyl (Boc) group (**3i**) gives the de*tert*-Butyloxy carbonyl product (**3b**) in 56% yield. Halogen (-F) substituted indolin-2-ones produced the corresponding products **3j** in moderate yield. The **3k** with a bromine (Br) group on phenyl and a butyl group on the nitrogen atom, was also obtained in good yield. Meanwhile, the **3k** is used to prepare a series of isoindigo-based low-band gap copolymers, such as, Thieno[3,2-b][1]benzothiophene isoindigo[15]. Interestingly, meisoindigo (**3l**) that can be used for treatment of chronic myelocytic leukemia (CML)[13] was also obtained in 45% yield. And 5-fluoro-5'-methoxy-[3,3'-biindolinylidene]-2,2'-dione (**3m**) was also produced in 46% yield. This protocol provides a practical way to synthesise isoindigo derivatives with the advantages of readily commercially available materials and convenient operation process.

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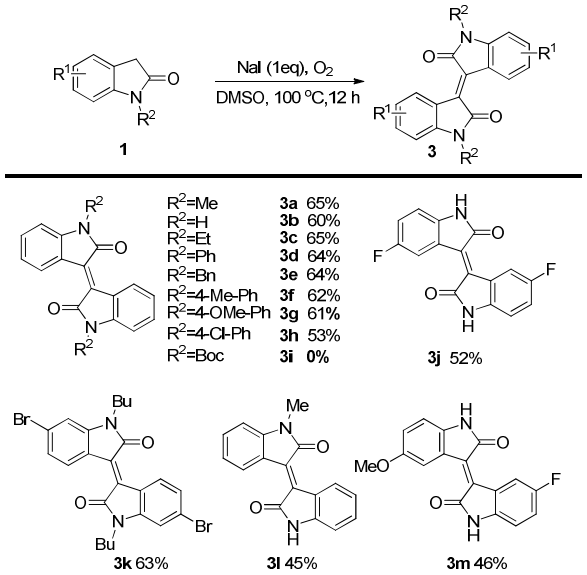
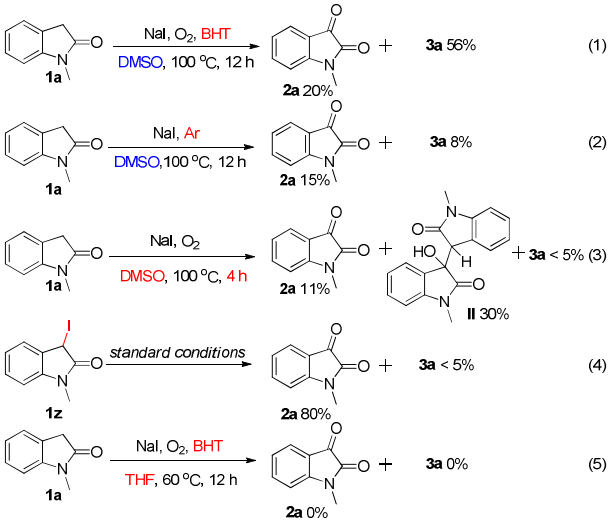


Scheme 3. Scope of the oxidation of indolin-2-ones to isoindigoes [a]. [a] Reaction conditions: **1** (0.1 mmol), NaI (0.1 mmol), O_2 (1 atm), 100 °C, DMSO (1 mL), 12 h.

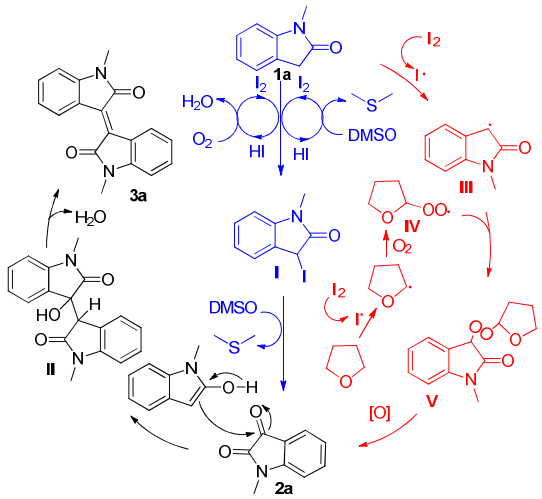
To gain insight into the mechanistic details, several control experiments were designed and conducted. When BHT was added to the system in DMSO, the desired products **2a** and **3a** were obtained in 20% and 56% yield (Scheme 4, eq 1), respectively. This result might allow us to exclude the possibility of radical pathway for the reaction in DMSO. When O_2 was replaced by Ar in DMSO, the products **2a** and **3a** were obtained in 15% and 8% yield (Scheme 4, eq 2), respectively, which indicated that the DMSO participated in the oxidation of indolin-2-one[22-24]. To our delight, when the reaction time was shortened to 4 h, 3-hydroxy-1,1'-dimethyl-[3,3'-biindoline]-2,2'-dione(**II**) was observed in 30% yield (Scheme 4, eq 3),



Scheme 4. Control experiments.

which manifested that the **II** may be the intermediate of the reaction. When 3-iodo-1-methylindolin-2-one (**1z**) was subjected to the reaction under standard conditions, **2a** could be obtained in 80% yield (Scheme 4, eq 4). This result indicated that **1z** might be the critical intermediate. On the other hand, when BHT was added to the system in THF, the reaction was completely suppressed (Scheme 4, eq 5), indicating the reaction in THF might involve radical process.

Based on the above results and the literatures, a plausible mechanism for this reaction was depicted in Scheme 5. First, I^- can be oxidized to I_2 by oxygen or DMSO. Then 1-methylindolin-2-one (**1a**) reacted with I_2 to give the intermediate[22, 23] **I**, which was oxidized to 1-methylindoline-2, 3-dione **2a** by DMSO[23, 24]. Then, the enolate of 1-methylindolin-2-one nucleophilic attacked **2a** to produce intermediate **II**, which was dehydrated and the final product was generated. On the other hand, iodine radical was generated from molecular iodine by heat or light. Subsequently, iodine radical abstracts a hydrogen atom from substrate **1a** to generate a key intermediate radical **III**. Meanwhile, iodine radical also abstracts α-hydrogen atom from the THF and the tetrahydrofuran-2-yl radical was generated. Peroxy radical **IV** was generated from tetrahydrofuran-2-yl radical and O_2[25]. Subsequently, the intermediate **V** was generated from the radical **III** and the radical **IV**. Then intermediate **V** can be oxidized to 1-methylindoline-2, 3-dione (**2a**)[9].



Scheme 5. Plausible reaction mechanism.

In conclusion, we have developed an efficient, metal-free, and practical method for the straightforward synthesis of isatins and isoindigoes from commercially available indolin-2-ones. The protocol featured with the use of inexpensive NaI as mediator, simple test procedure, wide substrates scope and high functional group tolerance. These isatins and isoindigoes are, meanwhile, presented as the key structural motifs in many biologically active molecules, and will find their applications in medicinal chemistry.

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Conflicts of interest

There are no conflicts to declare.

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