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The Power of Triplet and Singlet Oxygen in Synthesis: 2-Oxindoles, 3-Hydroxy-2-oxindoles, and Isatins from Furans

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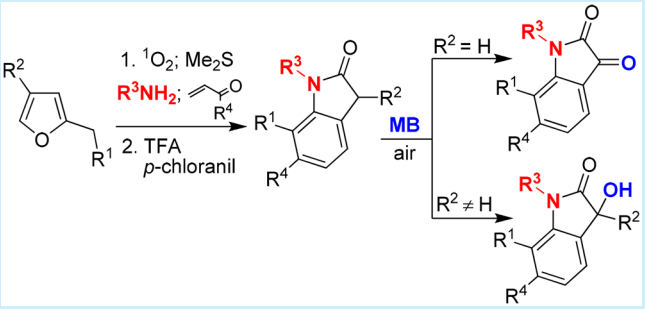
Supporting Information

ABSTRACT: A straightforward synthesis of substituted 2-oxindoles, 3-hydroxy-2-oxindoles, and isatins has been developed. Easily accessible furans were transformed into tetrahydropyranopyrrolones by a singlet oxygen initiated cascade reaction sequence. An acid-catalyzed rearrangement, followed by aromatization, gave access to a variety of 2-oxindole motifs, which were oxidized to 3-hydroxy-2-oxindoles or isatins using methylene blue as a radical initiator and molecular oxygen as a terminal oxidant.



2-Oxindoles, isatins, and 3-hydroxy-2-oxindoles constitute an important class of aromatic alkaloids present in numerous natural and non-natural products (Figure 1)[1] which exhibit remarkable

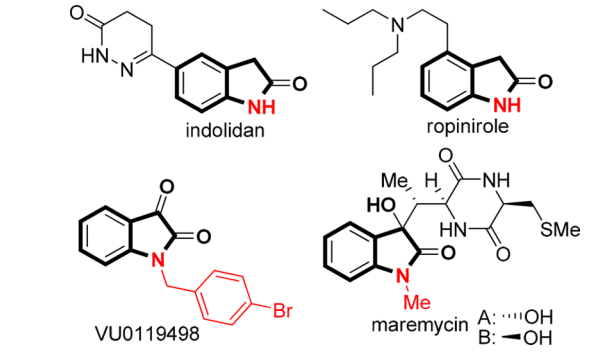


Figure 1. Examples of biologically active 2-oxindoles, 3-hydroxy-2-oxindoles, and isatins.

medicinal properties.[2] They are also valuable synthetic intermediates for the preparation of structurally complex drug candidates.[3] As a result, considerable efforts have been dedicated to the synthesis of these high value heterocycles.[4]

Many synthetic methodologies have focused on the synthesis of 2-oxindoles starting from substituted anilines,[5] phenyl acetic acids,[6] or indoles.[7] The majority of these methods, however, require advanced prefunctionalized precursors and/or utilize harsh reaction conditions. The synthesis of 2-oxindoles directly starting from simpler nonbenzenic components has rarely been studied.[8]

Aniline derivatives[9] and indoles[10] are also commonly used as the starting point for the synthesis of isatins and 3-hydroxy-2-oxindoles. Alternatively, nucleophilic additions to isatins have been extensively investigated as a means to synthesize 3-hydroxy-2-oxindoles.[11] Another straightforward approach to both these scaffolds is via the oxidation of oxindoles.[12] However, most of these oxidations implement relatively harsh reaction conditions, as well as metal catalysts or toxic reagents.

The development of a more flexible and mild protocol for rapid access to the title compounds is, therefore, highly desirable. Herein, we introduce an innovative approach for the synthesis of 2-oxindoles, 3-hydroxy-2-oxindoles, and isatins starting from readily accessible furans of type **1** (Scheme 1). It is known that the photooxygenation (singlet oxygen) of furans **1**, followed by treatment with Me_2S and primary amines, gives access to highly versatile intermediate β,γ-unsaturated γ-lactams of type **2**.[13] We have recently developed a protocol for the in situ transformation of these lactams into tetrahydropyranopyrrolones (THPP) **4** (Scheme 1) via a hetero-Diels−Alder reaction with α,β-unsaturated carbonyl compounds.[14] Rearrangement of these THPPs, catalyzed by $AlCl_3$, leads to dihydroindolones (DHI) **6**. Initially, we envisaged that oxindoles **7** could be accessed from THPP **4** by an acid-catalyzed rearrangement (e.g., **4** → **5**), followed by in situ aromatization (Scheme 1). Furthermore, we also anticipated that 2-oxindoles might be oxidized to the corresponding 3-hydroxy-2-oxindoles **8** and isatins **9** using methylene blue (MB) as a redox catalyst. Although MB is a dye and has, therefore, generally been employed as a photocatalyst,[15] our group recently unveiled its redox properties in the dark when applied to the oxidation of the γ-carbon of γ-lactams of type **2** under aerobic conditions (**2** → **3**, Scheme 1).[16] Since 2-pyrrolidinones **2** and oxindoles **7** have common structural features, we predicted that a similar protocol might be implemented for the oxidation of the α-carbon of oxindoles leading to the corresponding 3-hydroxy-2-oxindoles **8** and isatins **9** (Scheme 1).

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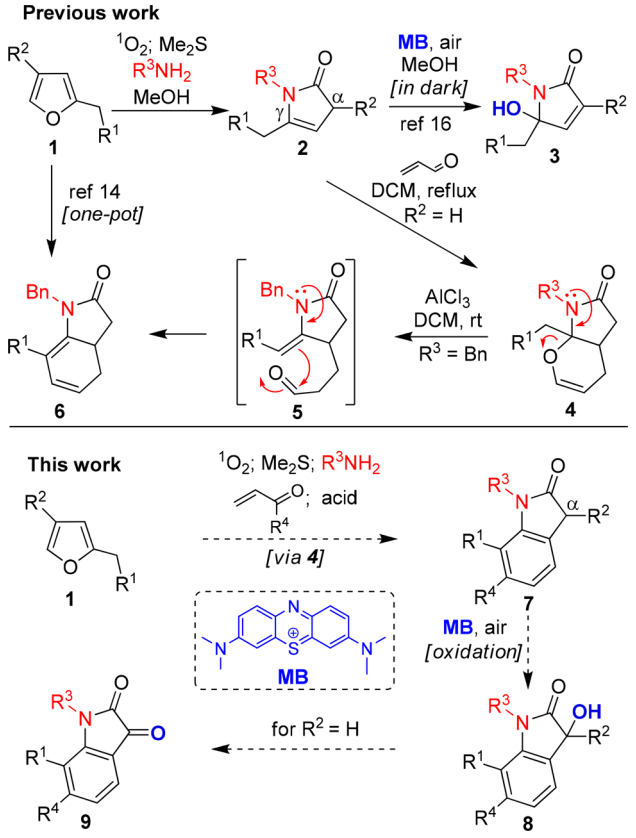
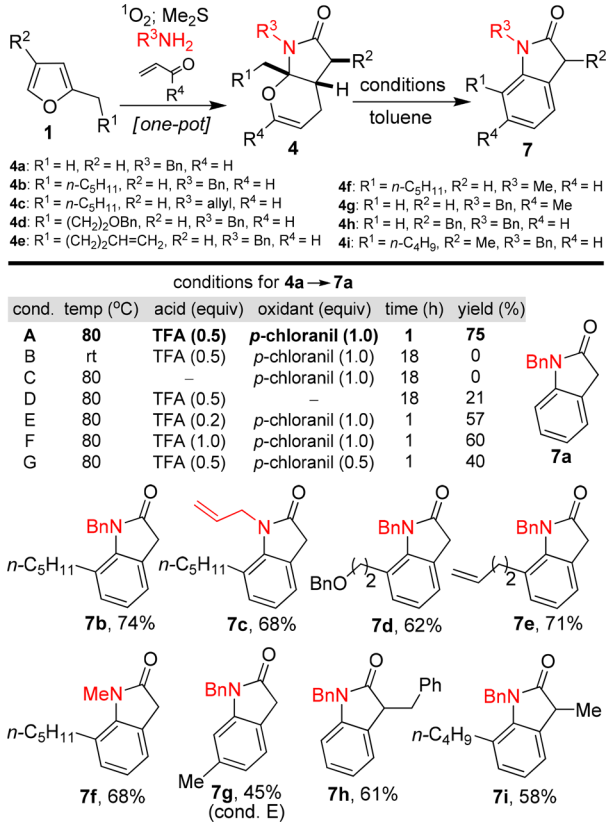
Scheme 1. Proposed Scenario for the Synthesis of 2-Oxindoles 3-Hydroxy-2-oxindoles and Isatins from Furans



Scheme 2. Two-Step Synthesis of 2-Oxindoles from Furans



conditions for **4a** → **7a**

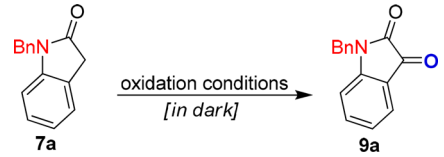
cond.	temp (°C)	acid (equiv)	oxidant (equiv)	time (h)	yield (%)
A	**80**	**TFA (0.5)**	***p*-chloranil (1.0)**	**1**	**75**
B	rt	TFA (0.5)	*p*-chloranil (1.0)	18	0
C	80	–	*p*-chloranil (1.0)	18	0
D	80	TFA (0.5)	–	18	21
E	80	TFA (0.2)	*p*-chloranil (1.0)	1	57
F	80	TFA (1.0)	*p*-chloranil (1.0)	1	60
G	80	TFA (0.5)	*p*-chloranil (0.5)	1	40

Initially, we investigated the first stage of the proposed transformation (**4** → **7**) using as a substrate the easily accessible cis-fused THPP **4a** (Scheme 2).[14] Treatment of **4a** with trifluoroacetic acid (TFA, 0.5 equiv) and the oxidant *p*-chloranil (1 equiv) in toluene at 80 °C led to exclusive formation of the desired oxindole **7a** in only 1 h and with 75% isolated yield (cond. A, Scheme 2). We chose toluene as the solvent due to the enhanced solubility of *p*-chloranil in it. It is notable that the reaction does not work at room temperature (cond. B) or without the presence of the acid (cond. C). The presence of the oxidant was also crucial for the reaction, since, without *p*-chloranil (cond. D), the product **7a** was isolated in just 21% yield. Different amounts of the acid (0.2 equiv, cond. E or 1 equiv, cond. F) or of the oxidant (0.5 equiv, cond. G) all resulted in lower isolated yields (40−60%).

To explore the scope of the reaction, different substrates of type **4** were synthesized from the corresponding furans **1** and tested under the optimized conditions A (Scheme 2). For compounds **4b−f** and **4h−i** bearing different R^1, R^2, and R^3 groups the reaction afforded the corresponding oxindoles **7b−f** and **7h−i** in good yields (58−74%). For compound **4g** (having a methyl group as R^4), milder reaction conditions could be used (0.2 equiv of TFA, cond. E, Scheme 2) in order to obtain the desired product **7g** (45% yield). In this case, using more acid leads to a mixture of isomers of the uncyclized compound of type **5** (Scheme 1) with the double bond having migrated to different positions.

We next turned our efforts toward examining the MB-induced oxidation of 2-oxindoles to 3-hydroxy-2-oxindoles and isatins. Various conditions were tested using compound **7a**, and in accordance with our previous studies,[16] the oxidation was promoted in a methanolic solution of MB under basic conditions (Table 1). Specifically, upon the addition of Et_3N (1 equiv) to a solution containing **7a** and a catalytic amount of MB (5 mol %) in MeOH, a partial decolorization of the solution was observed instantly, and after 18 h at room temperature, the desired isatin **9a** was isolated in 73% yield (entry 1). The reaction was performed in the dark, meaning that this is not a light-induced process. With lower amounts of MB or Et_3N, the reaction was significantly slower (entries 2−3), while, in the absence of either MB or Et_3N, the reaction did not work (entries 4−5). The presence of oxygen was essential for the oxidation step (entry 6).

Table 1. Optimization and Testing of the MB-Induced Oxidation of Oxindole 7a to Isatin 9a



entry	MB (mol %)	Et_3N (equiv)	solvent	conv (%) in 18 h	yield (%)
1	**5**	**1**	**MeOH**	**100**	**73**
2	3	1	MeOH	50	ND
3	5	0.5	MeOH	75	48
4	–	1	MeOH	0	–
5	5	–	MeOH	0	–
6	5	1	MeOH degassed	2	ND
7	5	1	CH_2Cl_2	9	ND

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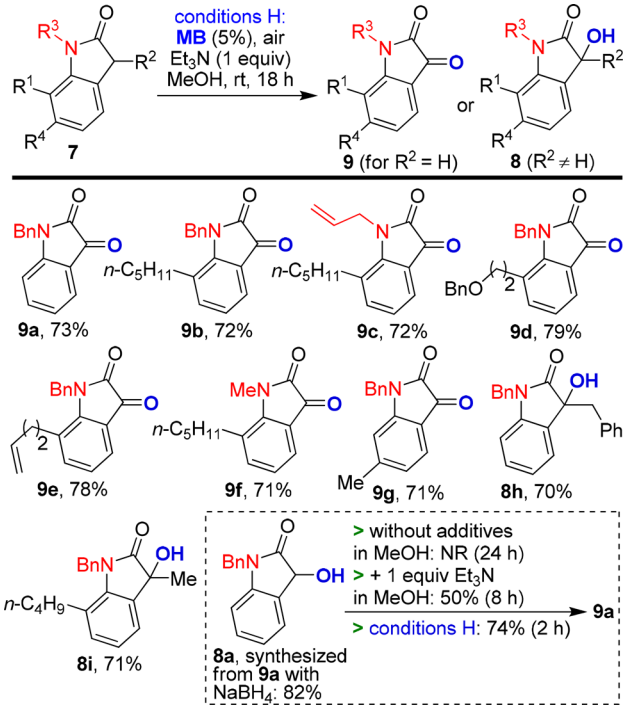
Furthermore, in the nonprotic solvent CH_2Cl_2, the conversion was low after 18 h (entry 7).

After validation of the optimal conditions (Table 1, entry 1), various 2-oxindoles were subjected to this new oxidation protocol with the results presented in Scheme 3. For compounds

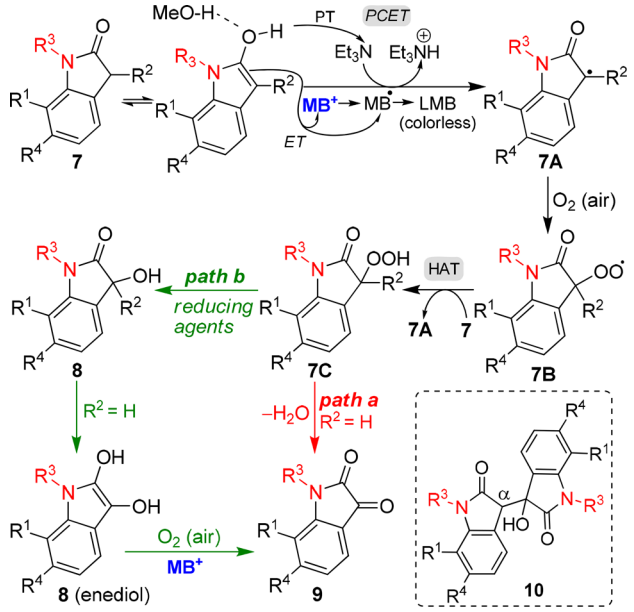
Scheme 3. MB-Induced Oxidation of 2-Oxindoles to Isatins and 3-Hydroxy-2-oxindoles



7a–g (R^2 = H), the reaction afforded the desired isatins **9a–g** effectively, regardless of the substituents at any of the R^1, R^3, and R^4 positions (71–79% isolated yield). When the same conditions were employed to 3-substituted 2-oxindoles **7h** and **7i**, the 3-hydroxy-2-oxindoles **8h** and **8i** were isolated as the sole products (70% and 71% isolated yields, respectively).

Since the oxidation proceeds only under basic conditions in the protic solvent MeOH, we propose a MB-induced proton coupled electron transfer (PCET)[17] initiation step (Scheme 4). Specifically, the enol tautomer of **7** might undergo proton transfer (PT) to the base and electron transfer (ET) to MB. This PCET step is responsible for the reduction of MB to the colorless leucomethylene blue (LMB), thus explaining the decolarization of the solution upon addition of the base. As a result, the radical intermediate **7A** is formed and may be trapped by the molecular oxygen leading to radical **7B**. A hydrogen atom transfer (HAT) from **7** to **7B** regenerates the propagating radical **7A** at the same time as affording hydroperoxide **7C**. From **7C**, two possible pathways are proposed for the formation of the final product **8** or **9**. In path a, when R^2 = H the dehydration of hydroperoxide **7C** leads directly to isatin **9**. In path b, the reduction of **7C** by a reducing agent present in the reaction solution (such as LMB and Et_3N) affords **8**. This hypothesis was supported by the observation that the 3-substituted oxindole **7i** was revealed to have formed a mixture of the corresponding hydroperoxide of type **7C** and product **8i**, in a 3:2 ratio, after just 1 h of reaction [see Supporting Information (SI)]. Since **8i** was the sole product after 18 h of reaction, it is reasonable to assume that the intermediate hydroperoxide is reduced to the final product **8i**

Scheme 4. Plausible Reaction Mechanism



under the reaction conditions. Indeed, treatment of isolated hydroperoxide **7C** (starting from **7i**) with Et_3N (1 equiv) in MeOH for 18 h afforded **8i** and the *N*-oxide of Et_3N (see SI).

When R^2 = H, isatins **9** can be obtained via the enediol form of **8**. Since enediols are prone to aerobic oxidation, **8** can be readily oxidized to **9** by molecular oxygen without the involvement of MB. Extra support for this assessment is derived from the fact that 3-hydroxy-2-oxindole **8a** (synthesized by reduction of **9a** with $NaBH_4$) was transformed to the corresponding isatin **9a** when subjected to Et_3N (1 equiv) in MeOH without the presence of MB (8 h, 50% yield, Scheme 3). Employing MB in this step accelerates the oxidation process via another radical propagating cycle (Scheme 4, R^2 = OH) affording **9a** in just 2 h (cond. H, 74% yield, Scheme 3).

It is notable that during the early stages of the oxidation of 3-unsubstituted 2-oxindoles **7a–g** (2 h), the formation of the corresponding dimeric compounds of type **10** (Scheme 4) was observed, as a result of the condensation of isatins **9** with the unreacted oxindoles **7**. However, these dimers were finally consumed by the reaction producing the corresponding isatins as the sole products. This consumption was achieved either via a reverse aldol reaction, followed by re-entry into the reaction sequence described above, or by the MB-induced oxidation of the dimer's α-position to the corresponding hydroperoxide followed by C–C bond cleavage with concomitant expulsion of water. The fact that we did not observe the formation of any intermediate hydroperoxide in these cases (R^2 = H) means that the expulsion of water must occur very rapidly independent of whether it is the dimer or monomer that is oxidized by MB.

In conclusion, a general and highly versatile methodology for the synthesis of substituted 2-oxindoles, 3-hydroxy-2-oxindoles, and isatins has been presented herein. 2-Oxindoles could be easily obtained (two steps) from a variety of readily accessible furan precursors, under mild and atom-economic conditions, using sustainable singlet oxygen chemistry. The synthesis of 3-hydroxy-2-oxindoles and isatins was accomplished via a metal-free, MB-initiated, but not light-dependent, oxidation of the corresponding oxindoles wherein molecular oxygen was the terminal oxidant.

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■ ASSOCIATED CONTENT

Supporting Information

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Detailed experimental procedures and spectral data (PDF)

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Notes

The authors declare no competing financial interest.

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