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Synthesis of Functionalized 6-Hydroxy-2-oxindole Derivatives by Phenoxide Cyclization

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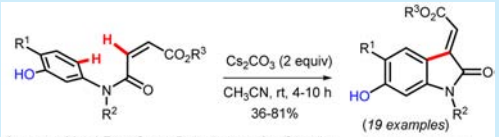
Supporting Information

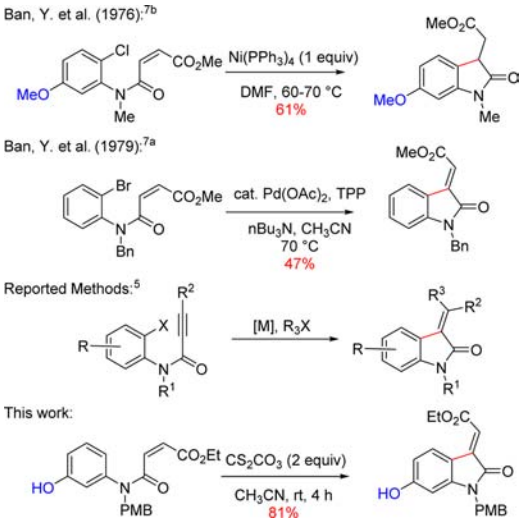
ABSTRACT: An apparent intramolecular cross-dehydrogenative coupling of *N*-(3-hydroxy)monoanilide of maleic esters comprising base promoted phenoxide cyclization and subsequent base-mediated aerobic oxidation was developed to synthesize a variety of 2-(6-hydroxy-2-oxoindolin-3-ylidene)-acetate derivatives. The isolation of intermediate cyclized products during the large scale reactions and their ready dehydrogenation with 1 equiv of base support this proposed two-step path.



Apparent Metal-Free Cross-Dehydrogenative Coupling involving an intramolecular phenoxide Michael addition followed by base mediated-aerobic oxidation

The indolin-2-one core is a frequently found substructural unit in the indole class of alkaloids and an important structural motif in pharmaceutically relevant small molecules.[1] In addition, the 3-methyleneindolin-2-one derivatives are very popular substrates employed widely in various (organo)catalytic transformations and cycloadditions, especially in the realm of diversity oriented synthesis and drug discovery.[2] The 3-alkylideneindolin-2-one derivatives in general are prepared from corresponding isatines either by Wittig homologation or by condensation with active methylene groups.[3] The methods for directly constructing the 3-alkylideneindolin-2-one core include the condensation of anilines with carbonyl compounds such as diethyl ketomalonate, oxalyl chloride, or chloral hydrate, mediated by strong acids/bases.[4] The metal-catalyzed intramolecular coupling of suitably functionalized *o*-haloanilides is another direct approach in this regard (Scheme 1).[5]

Scheme 1. Selected Approaches for 3-Alkylideneindolin-2-one



A literature search has revealed that the corresponding 6-methoxy-3-alkylidene derivative was first prepared in 1976 by Mori and Ban (a report that has gone largely unnoticed) employing a [Ni]-mediated intramolecular Heck-type coupling of *N*-(2-chloro)monoanilide of maleic esters.[7] Later, in 2004, William et al. reported the widely used method for synthesis of a similar derivative by following the classical Wittig 2-carbon homologation of the 6-methoxyisatisine.[8] Otherwise, it was interesting to note that even the synthesis of 6-hydroxy-2-oxindoles is quite rarely found in the literature and has been mainly limited to the patents that include also the parent 6-hydroxyisatine.[9] Despite the fact that there are several elegant methods based on tandem radical cyclization of *N*-arylacrylamides that appear often for 3,3-disubstituted oxindoles synthesis, rarely has a 6-hydroxy/6-alkoxy-2-oxindole been synthesized.[10]

This, taken together with the fact that there are a good number of natural products having 6-hydroxy and 6-methoxy-2-oxindole moieties present (Figure 1), has motivated us take up the problem

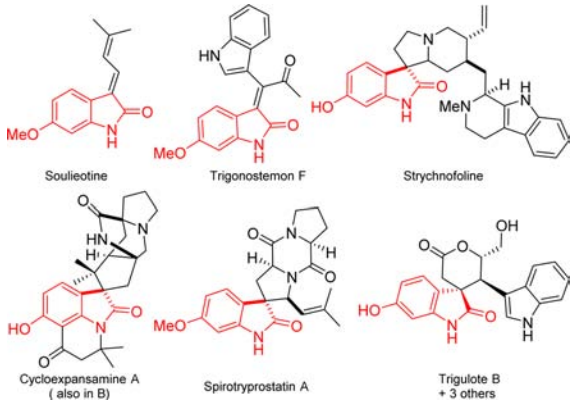


Figure 1. Natural products having 6-hydroxy-/6-methoxy-2-oxindole core.

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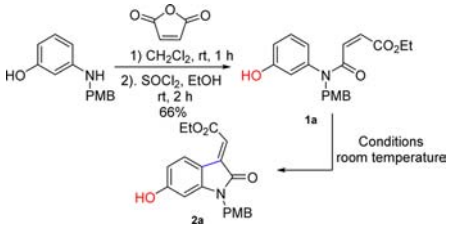
of developing a milder approach for the synthesis of 6-hydroxy-2-oxindole derivatives with a particular emphasis on the 2-(6-hydroxy-2-oxoindolin-3-yl)acetate that was required immediately as a part of the trigolutes total synthesis. Considering the optimal positioning of the requisite hydroxyl group *para* to the newly forming C−C bond in the product, we wondered about the possibility of a phenoxide cyclization. The intramolecular alkylation of phenoxide ions undergoing geminal cyclization first reported by Winstein and Baird is one of the classical methods for the synthesis of 4,4′-spirocyclohexadienones with widespread application in the synthesis of natural products.[11] However, the reports on the phenoxide intramolecular vicinal cyclization leading to the benzannulation are limited and so is the intramolecular Michael addition of the phenoxide anions. In this manuscript, we document a classical phenoxide cyclization comprising an intramolecular Michael addition leading to the 6-hydroxy-3-alkylideneindolin-2-one core.

To explore the feasibility of this proposed strategy, the model maleic anilide **1a** was prepared by treating *N*-PMB protected 3-hydroxy aniline with malice anhydride in DCM followed by esterification. Previous work on anionic phenolic cyclization demonstrated that the nature of the base can influence the outcome of the phenolate-mediated intramolecular Michael addition.[11] A successful realization of this reaction has required substantial optimization of the base and solvents. The results are summarized in Table 1. Initially, bases such as NaH and ^{t}BuOK

Table 1. Optimization of Reaction Conditions[a,b]



entry	reagent	solvent	yield (%)
1	NaH	THF	21
2	*t*-BuOK	CH_3CN	48
3	Li_2CO_3	CH_3CN	no reaction
4	Na_2CO_3	CH_3CN	no reaction
5	K_2CO_3	CH_3CN	no reaction
6	Cs_2CO_3	CH_3CN	81
7	Cs_2CO_3	THF	62
8	Cs_2CO_3	DMF	72
9	Cs_2CO_3	DMSO	76
10	Cs_2CO_3	CH_2Cl_2	no reaction
11	Cs_2CO_3	toluene	no reaction
12[b]	Cs_2CO_3	CH_3CN	80

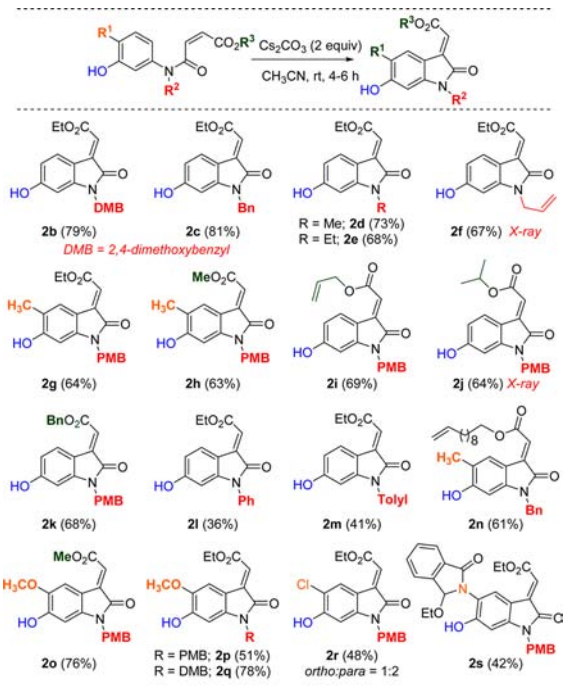
[a]Reaction conditions: **1a** (1 equiv), base (2 equiv), solvent (3 mL for 100 mg), 4 h. [b]In the presence of QuadraPure DMA (1:1 w/w with respect to the amide **1a**).

that are commonly used for phenoxide cyclization have been examined. In both cases, the formation of a new product was observed. Interestingly, this product was identified as 6-hydroxy-3-alkylidene derivative **2a** which presumably results from the base-mediated aerobic oxidation of the initially formed Michael product.[12]

Otherwise, in both instances, the amide hydrolysis was found to be the major event. To avoid this competing amide hydrolysis reaction, we examined the compatibility of mild carbonate bases such as Li_2CO_3, Na_2CO_3, K_2CO_3, and Cs_2CO_3. The employed conditions involve the use of 2 equiv of base and acetonitrile as the solvent and the stirring of the reaction mixture at rt. As reported in Table 1, out of the four bases employed (Table 1, entries 3−6), the results with Cs_2CO_3 are extremely rewarding. Unlike with the other three bases where the starting anilide **1a** was intact, with Cs_2CO_3, we could see 100% conversion within 4 h at rt and obtained pure **2a** in 81% isolated yield. The *E*-configuration of the trisubstituted double bond in **2a** was established with the help of NMR spectral data analysis and confirmed unambiguously by the single crystal X-ray analysis. The successful realization of this apparent cross dehydrogenative coupling is quite interesting and complements the corresponding [Ni]-mediated (using stoichiometric amounts of Ni-salts) and also the [Pd]-catalyzed cross-coupling approaches. As a control, we examined this reaction in the presence of QuadraPure DMA (1:1 w/w with respect to the amide **1a**) (Table 1, entry 12), a known scavenger for metals such as Pd, Cu(I), Cu(II), Ni, Pt, etc. The dehydrogenative cyclization of **1a** proceeded as usual without any interference from the added metal scavenger. Next examined was the compatibility of other solvents with Cs_2CO_3 (Table 1, entries 7−11). The use of Cs_2CO_3 in nonpolar solvents such as CH_2Cl_2 and toluene resulted in no reaction. However, in polar solvents such as tetrahydrofuran, *N*,*N*-dimethylformamide, and DMSO, the reaction proceeded with lower yields (Table 1, entries 7−9). Interestingly, cyclization of **2a** employing oxidizing agents such as DDQ, PIFA, CAN, iodine, and a Lewis acid such as $ZnCl_2$ was found to be unsuccessful [see Supporting Information (SI) for full details].

The scope of the current cyclization reaction was examined by varying the electronic and steric properties of the reactants. All the reactions are carried out on a 100 mg scale. As shown in Scheme 2, a variety of substrates underwent cyclization to afford oxindoles in high yields. It was noted that a tertiary amide has to be used to ensure the smooth occurrence of the annulation reaction, because the reaction with NH-free anilide resulted in the hydrolysis of the starting anilides. Interestingly, in all the successful cases, the

Scheme 2. Substrate Scope



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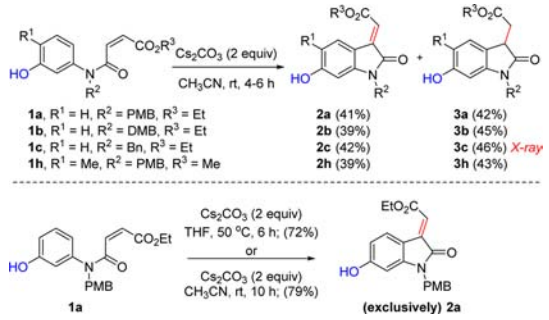
reactions proceed with complete *para*-selectivity, whereas in the case of **2r** an inseparable mixture (*ortho*/*para* = 1:2) was obtained. In the case of *N*-Ph and *N*-tolyl protected anilines, both the coupling with maleic anhydride and also the cyclization resulted in low yields. The substrates having trisubstituted alkenes were found to be noncompatible under the present cyclization conditions indicating that the steric crowding around the reacting C-center has a dramatic effect on the outcome. In control experiments employing the maleamides of 2-aminophenol and 3-methoxyaniline under the current conditions, the expected product was not produced or the starting compound was completely intact [see SI]. These results indicated that the presence of free −OH and its positioning are important for a successful cyclization.

Next the practicality of this reaction was examined by conducting the cyclization of **1a**−**1c**, **1h** on the 10 g scale under similar conditions. Interestingly, in all the cases, along with the final methylene derivatives **2a**−**2c**, **2h** the intermediate Michael products **3a**−**3c**, **3h** were also obtained in good proportions (Scheme 3).

Scheme 3. Substrate Scope on Gram Scale

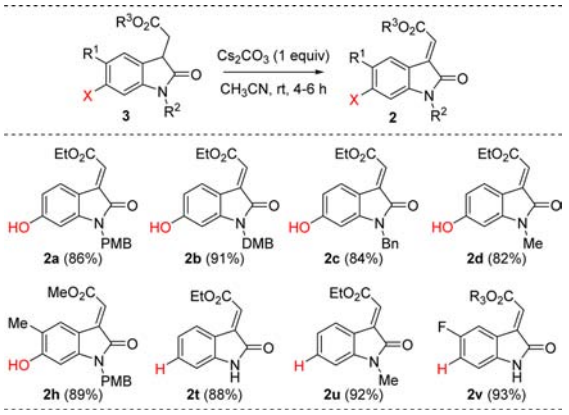


To address the issue of selectivity toward either of these products on large scales, the cyclization of **1a** has been examined under different conditions on a 5 g scale. To this end it was realized that either heating the reaction at 50 °C in THF as a solvent (6 h, 72%) or carrying the cyclization of **1a** under standard conditions employing 2 equiv of base in acetonitrile (with additional 25% acetonitrile) for a prolonged time (10 h, 79%) worked well and gave exclusively the alkylidene oxindole (Scheme 3).

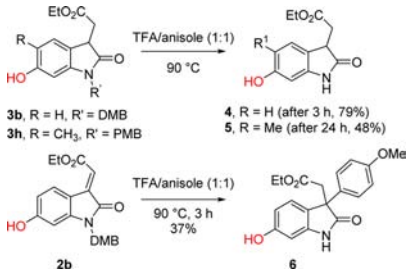
This revealed that the formation of the apparent cross-dehydrogenative products results from a stepwise intramolecular phenoxide Michael addition followed by a base-mediated aerobic oxidation. As a control, we treated these intermediate products **3a**−**3c**, **3d**, **3h** with 1 equiv of Cs_2CO_3 under similar conditions and obtained the anticipated methylene derivatives **2a**−**2c**, **2d**, **2h** in excellent yields (Scheme 4). Further, when the known 2-(2-oxoindolin-3-yl)acetates **3t**−**3v** were exposed to the current conditions, the corresponding methylene derivatives **2t**−**2v** were obtained in 88−93% yield. This suggested that the presence of *para* phenolic −OH is not essential for the present base-mediated aerobic oxidation.

Next, in order to show the utility of these oxindoles in total synthesis or any other methodology applications, we prepared the *N*-deprotected oxindoles **5** and **6** using TFA in anisole.[13] Interestingly, in the case of the alkylidene oxindole **2b** deprotection using TFA in anisole, the anisole added product **6** was obtained in low yield (Scheme 5).

Scheme 4. Substrate Scope for Dehydrogenation with Cs_2CO_3



Scheme 5. Synthesis of *N*-Deprotected Oxindoles



In summary, a simple access for the synthesis of 6-hydroxy-3-alkylideneoxindoles has been developed by employing a base-mediated intramolecular phenoxide cyclization of the *N*-(3-hydroxy)monoanilide of maleate esters. The reaction proceeds smoothly at rt and is effective in large scale synthesis. These rare and highly functionalized cyclized products are suitable for further elaborations with potential implications in the diversity oriented synthesis. The simplicity of the current reaction is an attractive aspect and has the potential to evolve as a reliable disconnection in the total synthesis of natural products having the 6-hydroxy-2-oxindole core.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b03048.

Detailed experimental procedures; characterization data for all the new compounds (PDF)
Crystallographic data (CIF, CIF, CIF)

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Notes

The authors declare no competing financial interest.

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