# Potassium *tert*-Butoxide-Mediated Condensation Cascade Reaction: Transition Metal-Free Synthesis of Multisubstituted Aryl Indoles and Benzofurans

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**Supporting Information** 

**ABSTRACT:** An efficient and facile method to synthesize valuable disubstituted 2-aryl indoles and benzofurans in good yields has been demonstrated, based on a *tert*-butoxide-mediated condensation reaction involving a vinyl sulfoxide intermediate. Products are obtained from N- or O-benzyl benzaldehydes using dimethyl sulfoxide as a carbon source. The methodology features a wide functional group tolerance and transition metal-free environment. Preliminary mechanistic studies suggest that the reaction involves a tandem aldol reaction (Michael addition (Achydracylforylation (isomorization)).



reaction/Michael addition/dehydrosulfenylation/isomerization sequence through an ionic protocol.

**S** ubstituted indoles<sup>1</sup> and benzofurans<sup>2</sup> are frequently encountered in various biologically active natural products, as well as in pharmaceuticals and other organic materials. Among these, 2-aryl multisubstituted derivatives,<sup>3,4</sup> especially indoles, have been the subject of much cooperative research as a result of the synthetic challenges that remain and the diverse biological properties that can be obtained from these compounds (for examples, see Scheme 1). Traditional synthetic approaches to the





synthesis of 2-arylindole include the Fischer, Larock, and Bartoli methods.<sup>5</sup> Recently, the exploration of newer flexible methodologies for the highly efficient syntheses of these biologically active structures has gained significant attention.<sup>6</sup> Two main strategies through direct C–H functionalization with transition metals have been developed: direct coupling annulation of anilines with C2 fragments (intermolecular and intramolecular)<sup>7</sup> and direct arylation for indole modification via direct coupling reactions.<sup>8</sup> However, in most cases, a stoichiometric amount of an expensive metal additive or oxidant is required.

Recently, few examples of the synthesis of 2-arylindole derivatives under transition metal-free conditions have been reported. One such method uses arynes as the aryl source, reacted with amines, 2H-azirines, or hydrazines under Lewis acid or Lewis acid-free conditions (Scheme 2a).<sup>9</sup> However, epoxide has been developed as C2 fragment to react with anilines forming 2arylindoles in the presence of Lewis acid (Scheme 2b).<sup>10</sup> ' In addition, the intramolecular amination reaction of anilines with different oxidants was a direct approach to aryl indole synthesis (Scheme 2c).<sup>11</sup> Very recently, potassium *tert*-butoxide (*t*-BuOK) was employed as an initiator in various types of coupling reactions, which provided an effective method for the direct silvlation<sup>12</sup> and arylation<sup>13</sup> of indoles. Yan developed an intramolecular coupling reaction of tertiary amines and ketones with t-BuOK to form 2-arylindoles via a radical pathway (Scheme 2d).<sup>14</sup> Even so, there remains a need to develop new, generic, and convenient transition metal-free strategies for synthesizing aryl indoles using other pathways.

Meanwhile, sulfoxides are employed as versatile regents in various organic transformations,<sup>15</sup> such as Swern oxidation, Pummerer reaction, and Corey–Chaykovsky reaction. However, a sulfoxide undergoes pyrolysis upon heating to form alkene and sulfenic acid has been known for over a century,<sup>16,17</sup> which needs two steps for preparation (substitution and oxidation) from the initial carbonyl compounds.<sup>18</sup> Hence, more efficient methods based on sulfur strategies for the rapid synthesis of alkenes are still required. Recently, some examples to formation of both alkenes

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### Scheme 2. Synthesis of 2-Arylindoles under Transition Metal-Free Conditions



and aromatic compounds have been reported by using DMSO as a carbon source.<sup>19,20</sup> However, there are no examples of dehydrosulfenylation approaches that proceed through the in situ preparation of sulfoxides to generate heteroaromatic rings starting from carbonyl compounds. As part of our continued interest in benzylic C–H bond functionalization,<sup>21</sup> we herein report the transition metal-free condensation of *N*- or *O*-benzylic C–H bonds with aldehydes using DMSO as the carbon source through a cascade protocol including dehydrosulfenylation to furnish 2-aryl-3-methylindoles and benzofurans in good yields.

Initially, 2-(benzyl(methyl)amino)benzaldehyde 1a was selected as the model substrate to investigate the optimal conditions to form disubstituted 2-aryl indoles via this process, using DMSO as the solvent. Although this transformation may appear simple, there are aspects that require careful consideration. First, direct intramolecular coupling reactions between the carbonyl group and the benzyl group to form the C3-H indole under basic conditions could complete with the formation of the desired C3–C indole product.<sup>14,22</sup> Second, intermolecular coupling reactions between the intermediate vinyl sulfoxide and the nucleophile could occur.<sup>23</sup> Finally, the radical pathway with t-BuOK may lead to the synthesis of other arylheterocycles, especially in the presence of a tertiary amine.<sup>24</sup> To our pleasure, when 1a was reacted with DMSO using t-BuOK as the base, the desired annulation product 2a was obtained in 62% yield at 90 °C for 0.5 h (Table 1, entry 1). After screening a series of inorganic bases, t-BuOK proved to be the optimum candidate, as it resulted in higher yields and shorter reaction times (entries 2-4). When substituting the organic super base P<sub>4</sub>-t-Bu for t-BuOK, only a small yield of the desired product 2a was observed (entry 5).<sup>25</sup> Thereafter, the effect of the amount of base was examined, and it was determined that 2.5 equiv of the base produced similar results to those obtained from 3.0 or 4.0 equiv (entries 7-9). The results of solvent screening indicated that adopting a mixed solvent approach also did not enhance the product yield (entries 10-12). The effect of reaction temperature was assessed, and the data showed that the yield of 2a was increased to 82% when the reaction was performed at 60 °C (entry 13). The reaction

Table 1. Optimization of the Reaction Conditions for the Synthesis of  $2a^{a}$ 

Ĺ	$ \begin{array}{c}                                     $	DCH <sub>3</sub> <u>base</u> , solven tempt time		CH <sub>3</sub> Ph CH <sub>3</sub> <b>2a</b>
entry	base (equiv)	temp (°C)	time (h)	yield (%) <sup>b</sup>
1	<i>t</i> -BuOK (2.0)	90	0.5	62
2	NaH (2.0)	90	4	32
3	KHMDS (2.0)	90	24	15
4	<i>t</i> -BuONa (2.0)	90	4	52
5	P4-t-Bu (2.0)	90	24	trace
6	<i>t</i> -BuOK (1.0)	90	4	42
7	<i>t</i> -BuOK (3.0)	90	0.5	80
8	<i>t</i> -BuOK (4.0)	90	0.5	81
9	<i>t</i> -BuOK(2.5)	90	0.5	80
10	<i>t</i> -BuOK(2.5)	90	0.5	10 <sup>c</sup>
11	<i>t</i> -BuOK(2.5)	90	0.5	51 <sup>d</sup>
12	t-BuOK(2.5)	90	0.5	60 <sup>e</sup>
13	<i>t</i> -BuOK(2.5)	60	0.5	82
14	<i>t</i> -BuOK(2.5)	40	2	70
15	<i>t</i> -BuOK(2.5)	60	0.5	84 <sup>f</sup>
16	<i>t</i> -BuOK(2.5)	60	0.5	58 <sup>g</sup>
17	<i>t</i> -BuOK(2.5)	60	4	83 <sup>h</sup>
18	<i>t</i> -BuOK(2.5)	60	0.5	83 <sup>i</sup>

<sup>*a*</sup>Reaction conditions: 1a (0.2 mmol) and base in 2 mL of DMSO were stirred at the desired temperature in a glass vial with cap. <sup>*b*</sup>Isolated yields. <sup>*c*</sup>DMSO (1 mL), *t*-BuOH (2 mL). <sup>*d*</sup>DMSO (1 mL), toluene (2 mL). <sup>*e*</sup>DMSO (1 mL), THF (2 mL). <sup>*f*</sup>DMSO (3 mL). <sup>*g*</sup>DMSO (1 mL). <sup>*h*</sup>DMSO (1 mL). <sup>*i*</sup>With the presence of trace metals from the *t*-BuOK and DMSO.

concentration also had an effect on the product yield, such that employing 3 mL of DMSO gave the highest yield of 84%. Thus, the reaction conditions listed in entry 15 of Table 1 were optimal. In addition, applying these optimal conditions and in the presence of trace metals from the *t*-BuOK and DMSO, the desired product **2a** was obtained in a similar yield (83%), which ruled out a transition metal effect.

Subsequently, using the optimized conditions, the scope of ortho-N-substituted aryl aldehydes to which this process could be applied was investigated. As shown in Scheme 3, various aryl aldehydes possessing both electron-withdrawing and electrondonating substituents on the aromatic ring could participate in this transformation to afford the desired products in moderateto-good yields. The reaction was found to proceed when using benzaldehyde substrates substituted in different positions, to give the corresponding C4, C5, or C6 substituted 3-methyl-2-phenyl indoles (2b-2j). Notably, the effect of the electron density of the phenyl ring was evident because products 2c, 2e, and 2h possessing electron-withdrawing groups, were isolated in lower yields compared with those obtained using reactants possessing electron-donating groups. The substrate scope was further expanded to include diverse substituted tertiary anilines. Tertiary amines bearing o-, m-, or p-substituted phenyl rings in the benzyl group were screened, and the results showed that products 2i-2n could be obtained with 55-89% yields. Interestingly, the reaction of 1m under optimized conditions yielded 2m at 89%. It should be noted that the reaction in the presence of tertiary amine substrates possessing N-Et, N-Pr, N-Bu, or N-Bn substituents proceeded smoothly to give the desired *N*-alkyl indoles (2o-2r), although a slight decrease in yield was observed. The

Scheme 3. Aryl Aldehyde Substrates Screening To Form Aryl Indoles  $^a$ 



"Reaction performed on a 0.2 mmol scale in a glass vial with cap; yields of isolated products.

tetrahydroisoquinoline benzaldehyde **1s** was also examined and was found to produce the corresponding product **2s** in 78% yield.

Encouraged by these results, we further explored the scope of this transformation while synthesizing benzofuran products by slightly modifying the reaction conditions. As shown in Scheme 4, the desired product 4a could be obtained with 84% yield in the

# Scheme 4. Aryl Aldehyde Substrates Screening To Yield Aryl Benzofurans ${}^a$



"Reaction performed on a 0.2 mmol scale in a glass vial with cap; yields of isolated products.

presence of 2-(benzyloxy)benzaldehyde **3a** using this *t*-BuOK/ DMSO system in conjunction with an increased temperature of 100 °C and 4.0 equiv of *t*-BuOK. Diverse 2-aryl benzofuran scaffolds were also successfully constructed under these reaction conditions, although slightly lower yields were observed when the electron-donating group was changed to an electronwithdrawing group.

To demonstrate the synthetic utility of this process, derivatization reactions of 2,3-disubstituted indoles were performed (Scheme 5). When the *N*-methyl-2,3-disubstituted indole **2a** was reacted with 2-hydroxy-5-nitrobenzyl bromide, the tetrahydrochromeno[2,3-*b*]indole **5** was obtained in 74% yield.<sup>26</sup> This *t*-BuOK-mediated condensation reaction could also be performed on a gram scale with **2r** in 60% yield.

To better understand the mechanism of this reaction, a series of control experiments were designed and conducted (Scheme 6). Using the stoichiometric radical scavengers TEMPO or

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Scheme 5. Derivatization of 2a and Gram-scale Reaction of 2r







diphenylethene to trap this transformation, the desired product was observed with slightly decreased yields of 78% and 79%, respectively. This result suggests that the reaction is based on a base anion process, which is not in agreement with previous studies of *t*-BuOK and tertiary amine systems.<sup>24</sup> The reaction of 1a with DMSO- $d_6$  was subsequently investigated to gain insight into the carbon pathway. The desired products  $2a - d_2$  and  $2a - d_3$ were obtained in 60% and 19% yields, respectively. In addition, the desired deuterated product was not detected following the reaction of 2a with DMSO- $d_6$  under standard conditions, even prolonged reaction times. These results indicate that the methyl group was obtained from DMSO but not from t-BuOK. When the reaction was allowed to proceed for 5 min at room temperature under standard conditions, the desired product 2a was obtained in 10% yield along with the vinyl sulfoxide 6a in 50% yield. Furthermore, 2a was obtained when the key intermediate 6a was subjected to the same reaction conditions under an argon atmosphere. Finally, when CH<sub>3</sub>SO<sub>2</sub>CH<sub>3</sub> was substituted for DMSO under standard conditions, a trace amount of 2a was formed. It is therefore evident that an intermediate sulfoxide, but not a sulfone, is the key factor in realizing the completion of the overall reaction.<sup>23</sup>

Based on the experimental results and in combination with previous literature, a plausible reaction mechanism is proposed, starting from the methylsulfinyl carbanion species,<sup>27</sup> as shown in Scheme 7. This nucleophilic reagent adds to the aldehyde to form the  $\beta$ -hydroxyl sulfoxide. Thereafter, one molecule of water is

#### Scheme 7. Plausible Reaction Mechanism



released to yield the vinyl sulfoxide **6a** through an aldol condensation reaction. Subsequently, **6a** undergoes a Michael addition reaction to obtain the intermediate **6b**, which eliminates sulfenic acid (CH<sub>3</sub>SOH) at high temperatures by thermolysis to form alkene **6c**. Under basic conditions, this alkene rapidly isomerizes to form the desired indole product **2a**.

In summary, we have developed an efficient transition metalfree method for the synthesis of important disubstituted 2-arylindoles and benzofurans, using DMSO as the carbon source. This *t*-BuOK-mediated process provides a straightforward protocol that uses widely available starting materials. Various 2-aryl-3methylindoles and benzofurans were readily obtained in moderate-to-good yields under mild conditions. It is important to note that, in this reaction, DMSO functions not only as a solvent but also as a reactant for the in situ generation of a sulfoxide in the basic system. Mechanistic studies show that the reaction proceeds via a four-step sequence through an anion pathway that includes aldol condensation, Michael addition, dehydrosulfenylation, and isomerization reactions.

#### ASSOCIATED CONTENT

# Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b01093.

Experimental procedures, characterization data, and copies of <sup>1</sup>H and <sup>13</sup>C NMR spectra (PDF)

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#### Notes

The authors declare no competing financial interest.

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