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$K_2S_2O_8$-Mediated Arylmethylation of Indoles with Tertiary Amines via sp^3 C–H Oxidation in Water

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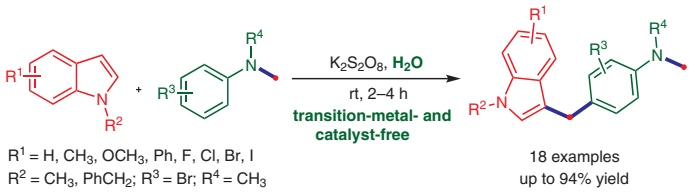

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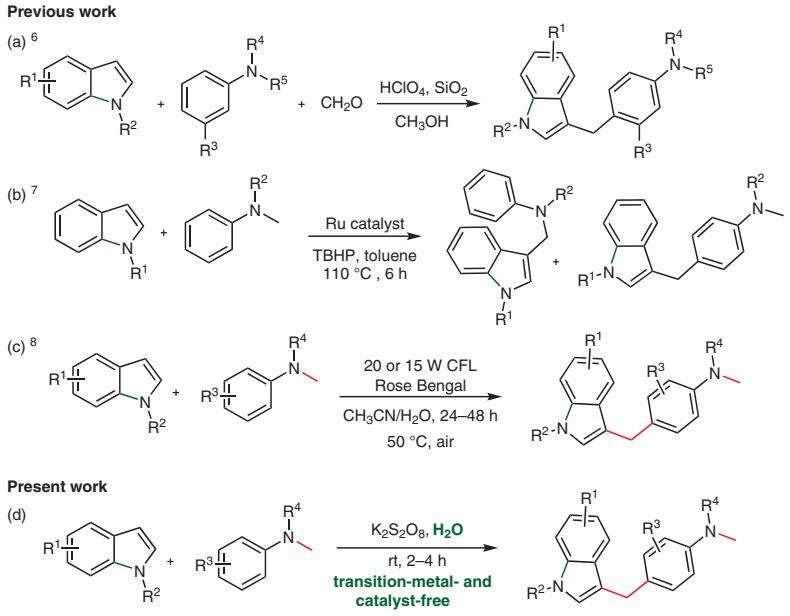
Abstract A transition-metal- and catalyst-free, highly efficient synthesis of 3-arylmethylindoles has been achieved using tertiary amines as both methylene (-CH_2-) transfer and arylmethylation agents and $K_2S_2O_8$ as a convenient oxidant. The key feature of this protocol is the utilisation of $K_2S_2O_8$ as an inexpensive and easy to handle radical surrogate that can effectively promote the reaction, leading to the formation of $C(sp^2)$–$C(sp^3)$–$C(sp^2)$ bonds via sp^3 C–H bond oxidation in water at room temperature in a one-pot procedure.

Key words alkylation, indoles, tertiary amines, heterocycles, $K_2S_2O_8$, radical oxidation

A plethora of sp^3 C–H bonds are present in organic compounds but they are extremely unreactive bonds. Thus, the direct functionalisation of sp^3 C–H bonds is a challenging task for synthetic organic chemists that has attracted considerable attention[1] because it does not require pre-functionalisation steps such as stoichiometric metalation and halogenation of the substrates. Particularly, a lot of effort has been devoted to the direct functionalisation of sp^3 C–H bonds α to a nitrogen, oxygen, or sulfur atom.[2] The process generally involves single electron transfer (SET) reaction and utilises organic peroxides such as benzoyl peroxide (BPO), *tert*-butyl hydroperoxide (TBHP), di-*tert* butyl peroxide (DTBP), and *tert*-butyl peroxybenzoate (TBPB) as oxidants to achieve couplings at sp^3 C–H centre.[3] However, these peroxides are required in an excess amount and work at only elevated temperatures, which limit their practicality.

3-Alkylindoles feature as key structural units in many natural products and pharmaceuticals exhibiting various biological properties such as antibacterial, antitumour, antioxidative, insecticidal, and antihelmintic activities.[4] Excellent reviews covering the synthesis and applications of indole derivatives are available.[4a,4b,5] The importance of 3-alkylindole derivatives is captivating, and consequently they have been target molecules in several organic syntheses.[5–8] Kumar and co-workers have reported the synthesis of 3-arylmethylindoles from indoles, formaldehyde, and tertiary amines using silica-supported perchloric acid ($HClO_4$–SiO_2) as a catalyst (Scheme 1a).[6] Che et al. reported the direct 3-arylmethylation of indoles by employing tertiary amines as both methylene (-CH_2-) transfer and arylmethylation agents using a ruthenium catalyst and *tert*-butyl hydroperoxide as an oxidant at 110 °C (Scheme 1b).[7] Very recently, the research groups of He[8a] and Weng[8b] have performed the same reaction under visible light irradiation using Rose Bengal as a photosensitiser (Scheme 1c). These reactions producing 3-arylmethylindoles proceed via an iminium ion intermediate generated from a tertiary amine by the oxidation of its sp^3 C–H bond α to the nitrogen atom. Generally, metals,[9] peroxides,[10] or inorganic oxidants[11] are required to generate an iminium ion by the oxidation of tertiary amines.

Recently, $K_2S_2O_8$ has been found to be a convenient and efficient radical surrogate to bring about synthetically useful chemical transformations under mild conditions.[12] It is a good oxidant to be employed in aqueous media. Moreover, owing to its low cost, easy handling and workability at room temperature, $K_2S_2O_8$ is advantageous over organic peroxides. Economical, environmental, and safety concerns have established water as the cleanest solvent. Only a few reports are available on the oxidation of sp^3 C–H bonds employing $K_2S_2O_8$ as a radical source.[13] In view of the above facts and in continuation of our studies on $K_2S_2O_8$-mediated organic synthesis,[13a,14] we envisaged the present convenient and highly efficient protocol for 3-arylmethylation of indoles in water (Scheme 1d). Although the previous metal-free works (Scheme 1c)[8] are elegant, they require Rose Bengal as a photosensitiser and tend to give somewhat low-



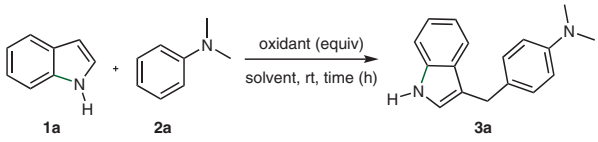
Scheme 1 Synthesis of 3-arylmethylindoles

er yields in a longer reaction time (24–48 h). The present work is catalyst-free, uses water as the solvent without addition of any co-solvent, and gives higher yields in a shorter reaction time (2–4 h) using a very simple procedure. Thus, this method is complementary and rather easier to execute than the previous works.[8]

To realise the envisaged protocol, a model reaction was performed with *N*,*N*-dimethylaniline (**2a**), indole (**1a**), and $K_2S_2O_8$ in CH_3CN at r.t., which delivered 87% yield of the desired product **3a** after 2 h (Table 1, entry 1). Encouraged by this result and from economical and environmental points of view, the same reaction was conducted in water; fortunately, it proceeded more efficiently to afford the product **3a** in 89% yield (entry 2). Other screened solvents such as DCE, DCM and DMSO were found to be far less effective than water (entry 2 vs. 3–5).

The optimum amount of $K_2S_2O_8$ was 1.5 equiv; the yield was significantly reduced on decreasing its amount from 1.5 to 1.0 equiv (Table 1, entry 2 vs. 6), whereas, the yield remained unchanged on using 2 equiv of the oxidant (entry 2 vs. 7). Other oxidants such as cerium(IV) ammonium nitrate (CAN), oxone, TBHP and DTBP were not as effective as $K_2S_2O_8$ (entry 2 vs. 8–11). To obtain the optimum yield, all the reactions were conducted with **1a** and **2a** in a 1:2 molar ratio, because the yield was considerably decreased on using an equimolar amount (entry 2 vs. 12), whereas the yield was unaffected when **1a** and **2a** were used in 1:2.5 ratio (entry 2 vs. 13). The reaction was quenched on addition of a radical scavenger 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) as the desired product **3a** was detected only in traces, which indicates that a radical intermediate is involved in the reaction (entry 14).

Table 1 Optimization of Reaction Conditions[a]



1a 2a 3a

Entry	Solvent	Oxidant (1.5 equiv)	Temp. (°C)	Time (h)	Yield (%)[b]
1	CH_3CN	$K_2S_2O_8$ (1.5)	r.t.	2	87
2	H_2O	$K_2S_2O_8$ (1.5)	r.t.	2	89
3	DCE	$K_2S_2O_8$ (1.5)	r.t.	4	78
4	CH_2Cl_2	$K_2S_2O_8$ (1.5)	r.t.	4	71
5	DMSO	$K_2S_2O_8$ (1.5)	r.t.	4	62
6	H_2O	$K_2S_2O_8$ (1.0)	r.t.	2	72
7	H_2O	$K_2S_2O_8$ (2.0)	r.t.	2	89
8	H_2O	CAN (1.5)	r.t.	4	76
9	H_2O	Oxone (1.5)	80	4	62
10	H_2O	TBHP (1.5)	80	4	55
11	H_2O	DTBP (1.5)	r.t.	4	67
12	H_2O	$K_2S_2O_8$ (1.5)	r.t.	2	44[c]
13	H_2O	$K_2S_2O_8$ (1.5)	r.t.	2	89[d]
14	H_2O	$K_2S_2O_8$ (1.5)	r.t.	2	traces[e]

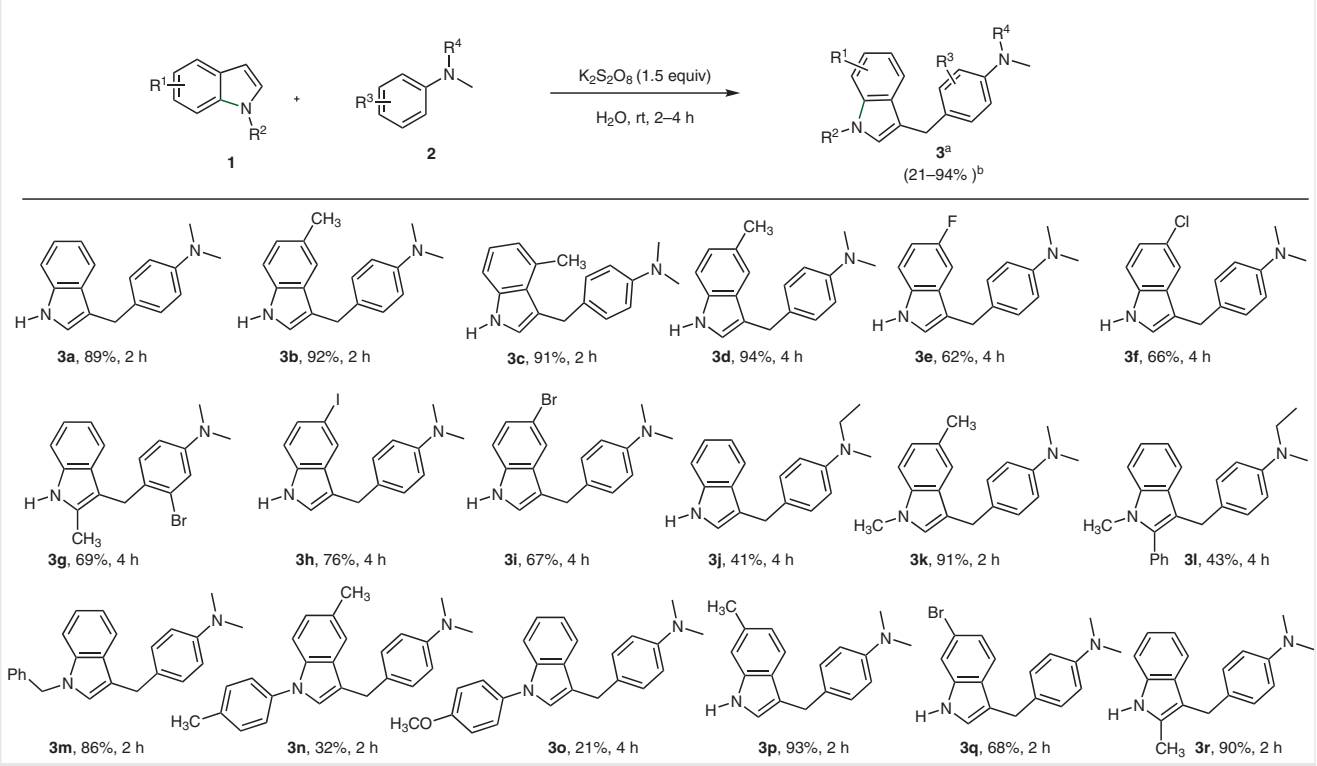
[a] Reaction conditions: **1a** (1.0 mmol), **2a** (2.0 mmol), oxidant (1–2 equiv), solvent (3 mL), stirred at r.t. for 2–4 h.
[b] Isolated yield of the pure product **3a**.
[c] Reaction was carried out with **1a** (1.0 mmol) and **2a** (1.0 mmol).
[d] Reaction was carried out **1a** (1.0 mmol) and **2a** (2.5 mmol).
[e] Reaction was quenched with TEMPO (4 equiv).

Employing the optimised reaction conditions (Table 1, entry 2), we examined the generality and scope of the present $K_2S_2O_8$-mediated synthesis of 3-arylmethylindoles **3** across a wide range of indoles **1** and tertiary amines **2**, incorporating various substituents such as CH_3, OCH_3, F, Cl, Br, I, and Et.[15] All of these smoothly reacted to afford 21–94% yields of the corresponding product **3** (Scheme 2), showing that the protocol is very mild and that considerable structural and functional group variations in the substrates **1** and **2** are well tolerated. The electronic and steric effects of the substituents present in **1** and **2** affect the efficiency of the reaction. The substrates bearing an electron-donating group on the aromatic ring appear to react faster and give slightly higher yields as compared to those having an electron-withdrawing group (Scheme 2, products **3b–d** and **3p** vs. **3e–i** and **3q**). *N*-Methylylindole has marginally higher yield than the corresponding unmethylated indole (Scheme 2, product **3k** vs. **3a**), whereas *N*-arylindoles have very low yields in comparison to *N*-alkylindoles (Scheme 2, products **3n** and **3o** vs. **3k–m**).

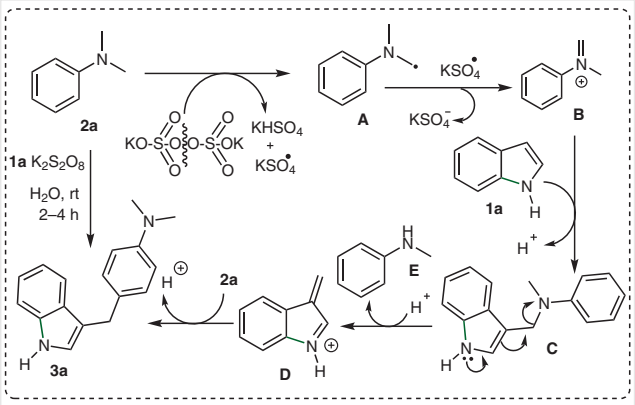
To evaluate the application of the present protocol in organic synthesis, a gram-scale synthesis of **3a** was conducted. Thus, the reaction of indole **1a** (10 mmol, 1.17 g) was performed with *N*,*N*-dimethylaniline **2a** (20 mmol, 2.42 g) in water (30 mL) at r.t. under the optimised reaction conditions. After completion of the reaction (2 h), the desired product **3a** was isolated in an excellent yield of 91% (2.27 g) without any decrease in efficiency as compared to that of the 1.0 mmol scale reaction.

In accordance with our observations and on literature precedent,[8a,13a] a plausible mechanistic pathway is proposed in Scheme 3. The $KHSO_4^{\cdot}$ radical, formed by homolysis of $K_2S_2O_8$, abstracts a hydrogen atom from *N*,*N*-dimethylaniline (**2a**) to generate an *N*,*N*-dimethylaniline radical **A**. A SET from radical **A** to $KSO_4^{\cdot}$ radical forms a highly reactive intermediate **B**, which undergoes nucleophilic attack by indole (**1a**) to give the corresponding aminomethylated indole **C**, and subsequently azafulvalene intermediate **D** with the loss of *N*-methylaniline (**E**).[16] The intermediate **D**, reacts with *N*,*N*-dimethylaniline (**2a**) to afford the final product **3a**.[17] The HRMS (EI) of the reaction mixture confirmed the formation of the intermediate **C** [HRMS (EI): *m*/*z* calcd for $C_6H_{16}N_2$: 236.1313; found: 236.1316]. This also supports the proposed mechanism.

In conclusion, we have developed an operationally simple, transition-metal- and catalyst-free highly efficient synthesis of 3-arylmethylindoles from indoles and tertiary amines using $K_2S_2O_8$ as a convenient oxidising agent in water. The reaction utilises tertiary amines as both methylene ($-CH_2-$) transfer and arylmethylation agents, $K_2S_2O_8$ as a



Scheme 2 Substrate scope for the synthesis of 3-arylmethylindoles. For experimental procedure, see ref.[15] [a] All compounds are known and were characterized by comparison of their spectral data with those reported in the literature[7,8] (see the Supporting information). [b] Yields of isolated pure compounds **3**.



Scheme 3 A plausible mechanism for the formation of 3-arylmethylindoles **3**

readily available, inexpensive, and easy to handle radical surrogate, and water as the greenest solvent. The protocol involves sequential formation of C(sp^2)–C(sp^3)–C(sp^2) bonds via sp^3 C–H bond activation in a one-pot operation at room temperature.

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0037-1610264.

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(15) **General procedure for the synthesis of 3-arylmethylindoles 3:** A mixture of *N*,*N*-dimethylaniline **1** (2.0 mmol), indole **2** (1.0 mmol), $K_2S_2O_8$ (1.5 equiv), and CH_3CN (3 mL) was taken in a flask and stirred at r.t. for 2–4 h (Scheme 2). After completion of the reaction (monitored by TLC), water (5 mL) was added and the mixture was extracted with ethyl acetate (3 × 5 mL). The combined organic phase was dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure. The resulting crude product was purified by silica gel chromatography using a mixture of hexane/ethyl acetate (4:1) as eluent to afford an analytically pure sample of product **3**.
Compound **3a** [see ref. 8]: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93 (s, 1 H), 7.52 (d, *J* = 7.9 Hz, 1 H), 7.34 (d, *J* = 8.1 Hz, 1 H), 7.14 (m, 3 H), 7.06 (m, 1 H), 6.85 (s, 1 H), 6.71 (d, *J* = 8.4 Hz, 2 H), 4.04 (s, 2 H), 2.93 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.1, 136.6, 129.7, 129.3, 127.6, 122.1, 121.9, 120.0, 119.3, 116.7, 113.1, 111.0, 41.1, 30.6. HRMS (EI): *m*/*z* calcd for $C_{17}H_{18}N_2$: 250.1470; found: 250.1473.

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