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Iodine-Mediated Domino Protocol for the Synthesis of Benzamides from Ethylarenes via sp^3 C–H Functionalization

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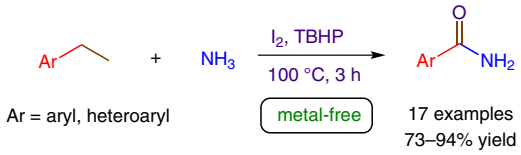
Dedicated to our mentor Prof. P. M. Bhate on the occasion of his 61st birthday



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Abstract An efficient, metal-free domino protocol for the synthesis of benzamides has been developed from ethylarenes using aqueous ammonia. The reaction proceeds through the formation of triiodomethyl ketone intermediate in the presence of iodine as the promoter and TBHP as an oxidant followed by nucleophilic substitution with aqueous ammonia, forming an amide. This operationally simple, functional-group-tolerant tandem approach provides an easy access to the broad range of biologically important benzamides.

Key words sp^3 C–H functionalization, benzamides, iodine, ethylarenes, *tert*-butyl hydroperoxide (TBHP)

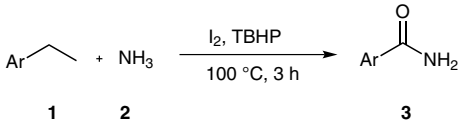
Amides are the significant structural units in numerous natural products, pharmaceuticals, biomolecules, and agrochemicals.[1–3] Additionally, they have been employed as starting materials for engineering plastics, detergents, and lubricants.[4] In particular, primary amides are the crucial intermediates in organic chemistry owing to their easy functional-group transformations into nitriles, primary amines, and heterocycles.[5] Furthermore, amide derivatives exhibit a broad spectrum of biological activities such as antifungal, antiprotozoal, anti-inflammatory, and antihypertensive.[6] Notably, aromatic and heteroaromatic amides are the key constituents of several established drugs namely frovatriptan, labetalol, leflunomide, nelfinavir, rilmazafone, and temozolomide.[6] On the background of the aforementioned applications of amides, various methods have been developed for their synthesis.

Conventionally, carboxylic acid or its derivatives such as acyl halides, mixed anhydrides, aldehydes, and esters are coupled with ammonia or its equivalent to give amides.[7] Primary amides are also prepared by reduction of acyl azides and acyl hydrazides,[8] hydration of nitriles in the presence of acids, bases, and transition-metal catalysts,[9] rearrangement of aldoximes using transition-metal catalysts,[10] metalloporphyrins-catalyzed oxidation of terminal alkynes,[11] ruthenium-catalyzed dehydrogenative coupling of primary alcohols with amines,[12] direct oxidation of benzyl amines[13] or benzyl alcohols,[14] aerobic oxidative amidation of methylarenes,[15] and palladium-catalyzed aminocarbonylation of aryl halides.[16] In view of the growing importance of green and sustainable chemistry in organic synthesis, several environment-friendly procedures for the synthesis of benzamides have also been developed. Recently, Wu et al.[17] reported I_2-mediated direct transformation of acetophenones and carbinols to benzamides using aqueous ammonia in water, whereas Narender et al.[18] used a combination of I_2 with NaN_3 in the presence of a base to prepare benzamides from acetophenones. Moreover, Wu and coworkers[19] synthesized benzamides from styrenes in the presence of TBHP. Similarly, Chen et al.[20] developed an efficient synthesis of benzamides from aldehydes and ammonium chloride using Cu_2O as the catalyst and TBHP as an oxidant. Likewise, Song et al.[21] prepared benzamides from phenylacetic acids and α-hydroxyphenylacetic acids with aqueous ammonia using Cu_2O as the catalyst in water.

However, in spite of their effectiveness these existing methods suffer from one or more drawbacks such as the use of metal-mediated catalysis, hazardous and expensive reagents, strong acidic or basic conditions, longer reaction times, higher reaction temperatures, incompatibility with functionalized substrates, low yield of products, and multistep synthesis which not only reduce process efficiency but also pose environmental problems.

Therefore, the development of a simple, green, and efficient process for the synthesis of benzamides is highly desirable. In this context, considering the practical advantages of domino reaction and with our continuous interest in the development of environment and eco-friendly protocols,[22] herein we report a new metal-free tandem approach for the

synthesis of benzamides **3** from ethylarenes **1** in the presence of I_2 and TBHP by employing aqueous ammonia (**2**, Scheme 1).

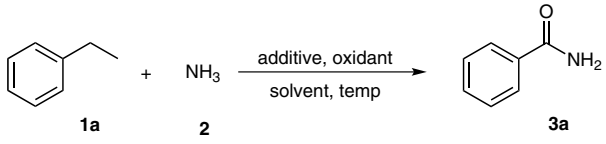


Scheme 1 I_2/TBHP-mediated synthesis of benzamides from ethylarenes

In order to optimize the reaction conditions for this one-pot oxidative amidation, the reaction between ethylbenzene (**1a**) and aqueous ammonia (**2**) using 0.2 equivalents of I_2 and 2.0 equivalents of TBHP as an oxidant was carried out at 60 °C for 3.0 hours to obtain benzamide (**3a**) in 12% yield (Table 1, entry 1). Use of 4.0 and 6.0 equivalents of TBHP resulted in slightly higher yields of the product (Table 1, entries 2 and 3). The reaction was then performed at 80 °C and 100 °C, whereupon yields of 34% and 45% were obtained (Table 1, entries 4 and 5), thereby indicating a significant role played by temperature in this reaction. We next varied the I_2 concentration from 0.3 equivalents to 1.5 equivalents using 6.0 equivalents of TBHP at 100 °C. The reaction with 0.3 equivalents of I_2 gave 51% yield of the product (Table 1, entry 6), whereas higher yields of 62% and 79% were achieved using 0.5 and 1.0 equivalents of I_2, respectively (Table 1, entries 7 and 8). Use of 1.1 equivalents of I_2 and 6.0 equivalents TBHP at 100 °C was found to be the optimum reaction conditions for this conversion resulting in 85% yield of the product (Table 1, entry 9). A slight drop in the yields was observed when the I_2 concentration was increased to 1.2 and 1.5 equivalents (Table 1, entries 10 and 11). The other common oxidants such as DTBP, TBPB, CHP, and H_2O_2 were also used for this reaction (Table 1, entries 12–15), but TBHP was found to be the most effective oxidant for this transformation. The reaction could not occur in the absence of I_2 (Table 1, entry 16), indicating that I_2 played a crucial role in the reaction. We also screened different additives such as NIS, KI, CuI, and TBAI for this reaction which resulted in low yields of the product (Table 1, entries 17–20). Further, various solvents like DMSO, H_2O, DMF, MeCN, and 1,4-dioxane were tested to check whether any of these produce favorable results. The reaction in DMSO did not form the desired product (Table 1, entry 21), whereas moderate yield (65%) of the product was obtained for the reaction in H_2O (Table 1, entry 22). The reactions in DMF, MeCN, and 1,4-dioxane could afford benzamide (**3a**) only in trace amounts (Table 1, entries 23–25).

With these optimized reaction conditions in hand, we explored the scope and limitations of this transformation by using substituted ethylarenes.[23] Ethylarenes bearing halogen substituents such as 2-F, 2-Cl, 4-F, 4-Cl, and 4-Br reacted smoothly with aqueous ammonia to offer the corresponding benzamides **3b–f** in yields ranging from 86–93% (Table 2, entries 2–6). Ethylarenes with electron-donating substituents such as 2-Me, 4-Me, 2-OMe, 4-OMe, and 3,4-di-OMe furnished the corresponding benzamides **3g–k** in good yields (73–81%, Table 2, entries 7–11). The reactions of ethylarenes **1l** and **1m** with an electron-withdrawing substituent such as NO_2 at the *ortho* and *para* positions resulted in formation of benzamides **3l** and **3m** in 90% and 94% yield, respectively (Table 2, entries 12 and 13). Similar-

Table 1 Optimization of Reaction Conditions[a]

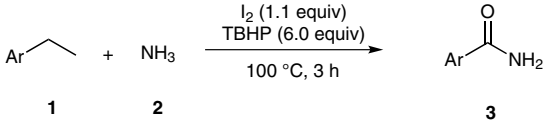


Entry	Additive (equiv)	Oxidant (equiv)[d]	Solvent	Temp (°C)	Yield (%)[e]
1	I_2 (0.2)	TBHP (2)	–	60	12
2	I_2 (0.2)	TBHP (4)	–	60	19
3	I_2 (0.2)	TBHP (6)	–	60	25
4	I_2 (0.2)	TBHP (6)	–	80	34
5	I_2 (0.2)	TBHP (6)	–	100	45
6	I_2 (0.3)	TBHP (6)	–	100	51
7	I_2 (0.5)	TBHP (6)	–	100	62
8	I_2 (1.0)	TBHP (6)	–	100	79
9	I_2 (1.1)	TBHP (6)	–	100	85
10	I_2 (1.2)	TBHP (6)	–	100	82
11	I_2 (1.5)	TBHP (6)	–	100	76
12	I_2 (1.1)	DTBP (6)	–	100	n.r.
13	I_2 (1.1)	TBPB (6)	–	100	n.r.
14	I_2 (1.1)	CHP (6)	–	100	60
15	I_2 (1.1)	H_2O_2 (6)	–	100	53
16[b]	–	TBHP (6)	–	100	n.r.
17	NIS (1.1)	TBHP (6)	–	100	35
18	KI (1.1)	TBHP (6)	–	100	28
19	CuI (1.1)	TBHP (6)	–	100	22
20	TBAI (1.1)	TBHP (6)	–	100	41
21[c]	I_2 (1.1)	TBHP (6)	DMSO	100	n.d.
22[c]	I_2 (1.1)	TBHP (6)	H_2O	100	65
23[c]	I_2 (1.1)	TBHP (6)	DMF	100	trace
24[c]	I_2 (1.1)	TBHP (6)	MeCN	100	trace
25[c]	I_2 (1.1)	TBHP (6)	1,4-dioxane	100	trace

[a] Reaction conditions: ethylbenzene (**1a**, 1.0 mmol), aq NH_3 (**2**, 10.0 mmol), additive (0.2–1.5 mmol), and oxidant (2.0–6.0 mmol) were heated at 60–100 °C for 3.0 h in sealed tube.
[b] TBHP (6.0 mmol) in the absence of I_2.
[c] I_2 (1.1 mmol), TBHP (6.0 mmol), and solvent (2.0 mL).
[d] DTBP = di-*tert*-butyl peroxide, TBHP = *tert*-butyl hydroperoxide, TBPB = *tert*-butyl peroxybenzoate, CHP = cumene hydroperoxide.
[e] Isolated yields; n.r. = no reaction. n.d. = not detected.

ly, 1-ethylnaphthalene also offered the corresponding amide **3n** in 87% yield (Table 2, entry 14). Notably, heteroarylethanes such as 2-ethylfuran, 2-ethylthiophene, and 3-ethylpyridine formed the corresponding benzamides **3o–q** in 76–81% yields (Table 2, entries 15–17).

Table 2 I_2/TBHP-Mediated Synthesis of Benzamides from Ethylarenes[a]



1 **2** **3**

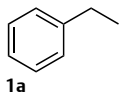
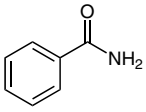
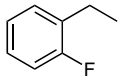
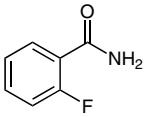
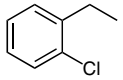
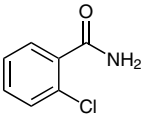
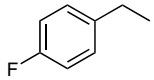
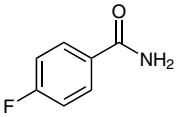
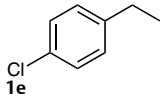
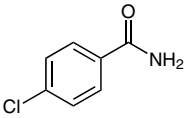
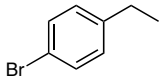
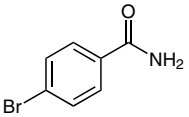
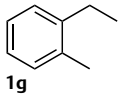
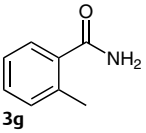
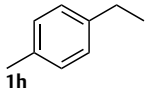
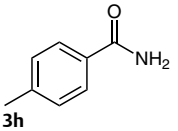
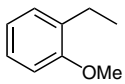
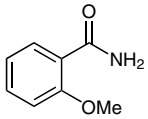
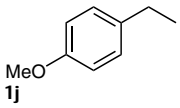
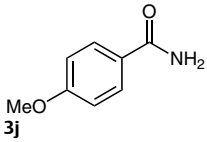
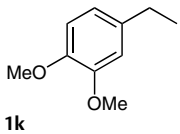
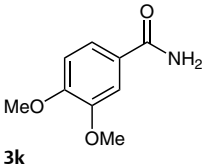
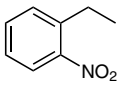
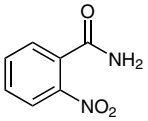
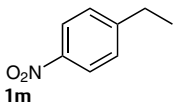
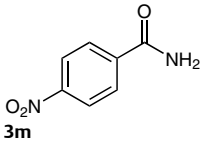
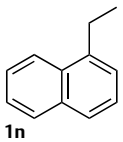
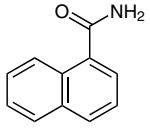
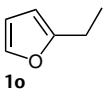
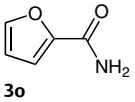
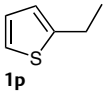
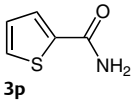
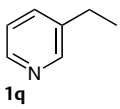
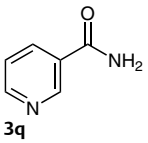
Entry	Substrate	Product	Yield (%)[b]
1	 **1a**	 **3a**	85
2	 **1b**	 **3b**	87
3	 **1c**	 **3c**	86
4	 **1d**	 **3d**	89
5	 **1e**	 **3e**	91
6	 **1f**	 **3f**	93
7	 **1g**	 **3g**	73
8	 **1h**	 **3h**	75

Table 2 (continued)

Entry	Substrate	Product	Yield (%)[b]
9	 **1i**	 **3i**	80
10	 **1j**	 **3j**	78
11	 **1k**	 **3k**	81
12	 **1l**	 **3l**	90
13	 **1m**	 **3m**	94
14	 **1n**	 **3n**	87
15	 **1o**	 **3o**	80
16	 **1p**	 **3p**	81
17	 **1q**	 **3q**	76

[a] Reaction conditions: ethylarene (**1**, 1.0 mmol), aq NH_3 (**2**, 10.0 mmol), I_2 (1.1 mmol), and TBHP (6.0 mmol) were heated at 100 °C for 3.0 h in sealed tube.
[b] Isolated yields.

A few controlled experiments (Scheme 2) were performed in order to confirm our proposed mechanism. To demonstrate the involvement of TBHP in the formation of triiodomethyl ketone (**B**), a key intermediate, ethylbenzene (**1a**) was reacted with I_2 and DMSO at 100 °C (Scheme 2, a). The reaction failed to produce the triiodomethyl ketone (**B**), proving that TBHP plays a crucial role in the formation of triiodomethyl ketone (**B**) through radical intermediates. When ethylbenzene (**1a**) was treated with TBHP in the absence of I_2 (Scheme 2, b), the reaction did not form acetophenone (**A**) thereby clearly highlighting the key role of I_2 in this reaction. Compound **1a** on reaction with I_2 and TBHP as an oxidant (Scheme 2, c) resulted in successive formation of acetophenone (**A**) and triiodomethyl ketone (**B**), an important intermediate, which was finally converted into benzamide (**3a**) in the presence of aqueous ammonia. These facts ascertained the requirement of I_2 as a promoter and TBHP as an oxidant. We have also carried out the reaction of ethylbenzene (**1a**) using a combination of I_2 with TBHP in the presence of DMSO as the solvent. We found that the reaction proceeded through the consecutive formation of acetophenone (**A**) and α-iodoacetophenone (**A'**) in the presence of I_2 and TBHP. α-Iodoacetophenone (**A'**) was finally converted into phenyl glyoxal (**C**) in the presence of DMSO via Kornblum oxidation (Scheme 2, d).

Based on our control experiments, a plausible mechanism for this transformation is presented in Scheme 3. Ethylbenzene (**1a**) is oxidized to acetophenone (**A**) by I_2/TBHP via a radical mechanism with 1-phenylethanol as an intermediate product. Formation of acetophenone was confirmed by TLC, GC–MS, and ^{1}H NMR spectroscopy. Acetophenone (**A**) on iodination is converted into triiodomethyl ketone (**B**). This key intermediate on amidation with aqueous ammonia forms benzamide (**3a**).

In conclusion, an iodine-promoted domino strategy for the synthesis of benzamides from simple unactivated ethylarenes has been developed. Use of an inexpensive additive, wide functional-group tolerance, good to excellent yields of the products, and environment-friendly conditions are the striking features of this protocol. We strongly believe that this metal-free tandem synthetic approach would be useful for the synthesis of complex molecules in the field of medicine and materials.

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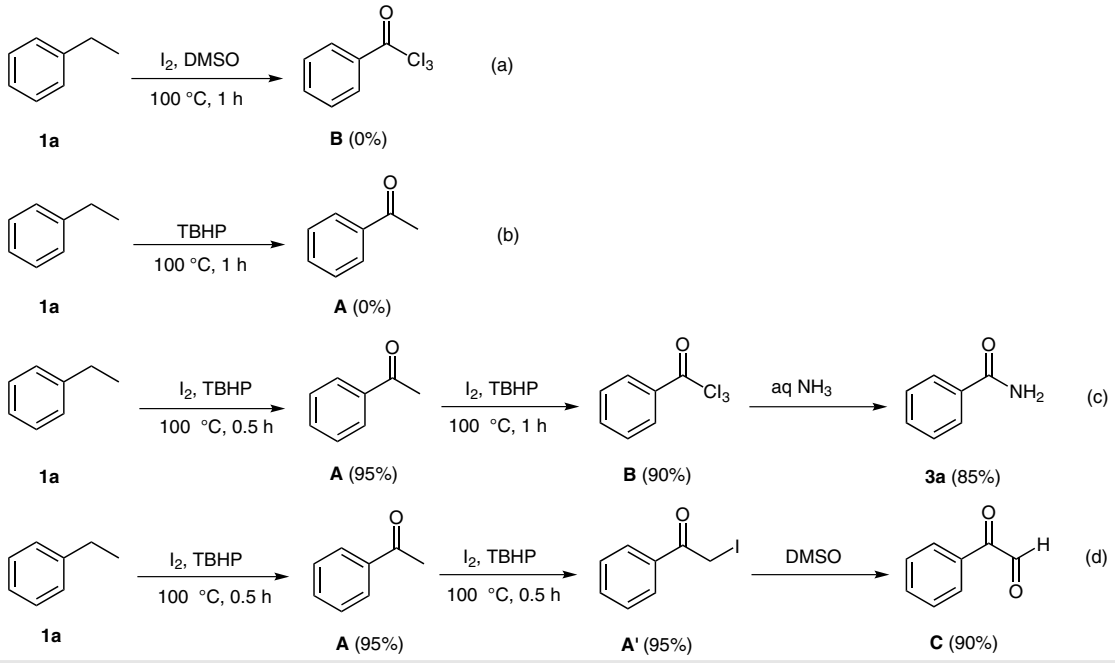
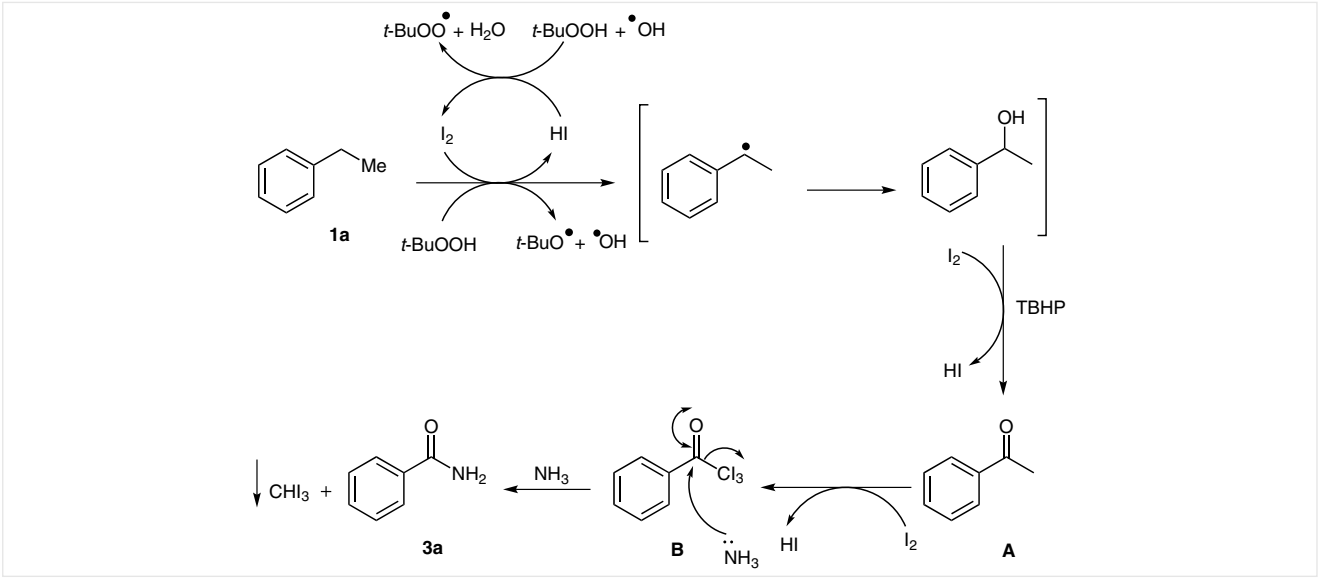
Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0034-1380210.



Scheme 2 Control experiments



Scheme 3 Plausible reaction mechanism

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(23) **General Procedure for the Oxidative Amidation of Ethylarenes**
A sealed tube equipped with a magnetic stirring bar was charged with ethylarene (**1**, 1.0 mmol), aq NH_3 (**2**, 25% aq solution, 10.0 mmol), I_2 (1.1 mmol), and TBHP (6.0 mmol, 70% aq solution) at r.t. The resulting mixture was heated to 100 °C for 3.0 h. After completion of the reaction (monitored by TLC), sat. $Na_2S_2O_3$ solution (10 mL) was added to the reaction mixture, and it was extracted with EtOAc (2 × 20 mL). The organic layer was washed with brine solution (20 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on 100–200 mesh silica gel using EtOAc–*n*-hexane (1:2) as the eluent to obtain the corresponding benzamide **3**.