2-Arylindoles: A New Entry to Transition Metal-free Synthesis of 2-Aminobenzophenones

Jin Yu, Hye Ran Moon, Beom Kyu Min, and Jae Nyoung Kim*

*Department of Chemistry and Institute of Basic Science, Chonnam National University, Gwangju 500-757, Korea. *E-mail: kimjn@chonnam.ac.kr*

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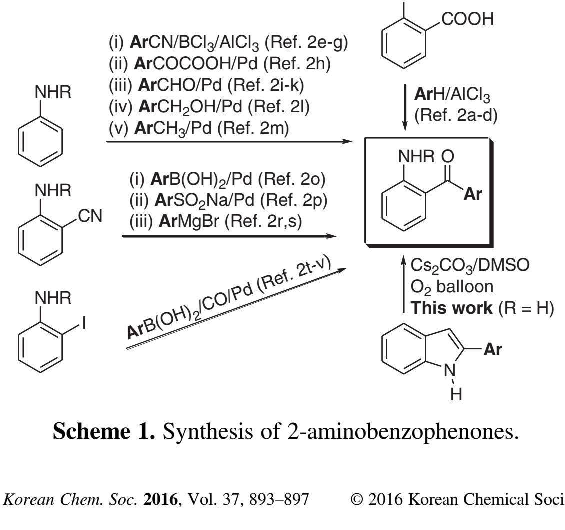
Various 2-aminobenzophenones were synthesized from readily available 2-arylindoles in DMSO under O_2 balloon atmosphere. The synthesis was carried out without the aid of a transition metal catalyst or moisture-sensitive organometallic reagents from 2-arylindoles.

Keywords: 2-Arylindoles, 2-Aminobenzophenones, Aerobic oxidation, Semipinacol rearrangement

Introduction

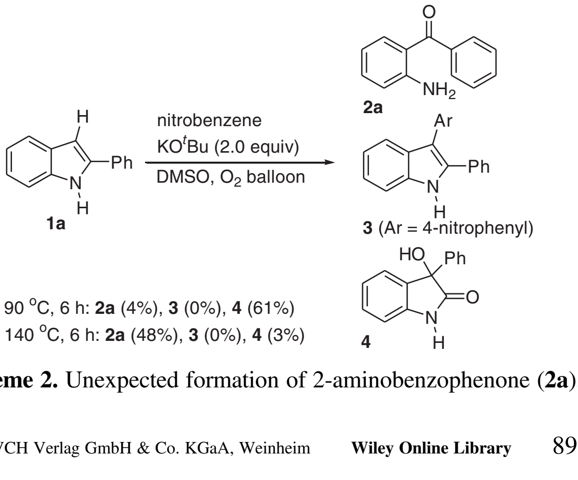
2-Aminobenzophenones are important building blocks for the synthesis of benzodiazepines,[1a] quinolines,[1b–d] quinazolines,[1e,f] and numerous biologically important compounds.[1g–k] Thus, considerable efforts have been made to develop an efficient synthetic method of these valuable compounds (Scheme 1).[2] Traditionally, 2-aminobenzophenones has been synthesized by Friedel-Crafts acylation between anthranilic acids and arenes[2a–d] or by the reaction between anilines and benzonitriles in the presence of Lewis acids.[2e–g] Ge and coworkers reported palladium-catalyzed decarboxylative *ortho*-acylation of acetanilides with α-oxocarboxylic acids.[2h] Later, palladium-catalyzed oxidative coupling reaction between anilides and aldehydes has been developed independently by Kwong,[2i] Wang,[2j] and Yu.[2k] The substrate scope of palladium-catalyzed oxidative coupling has been extended to benzyl alcohols by Yuan[2l] and toluene derivatives by Kwong.[2m] Su and coworkers reported palladium-catalyzed synthesis of 2-aminobenzophenones from 2-aminobenzonitriles with arylboronic acids or sodium arylsulfinates.[2o,p] Besides these methods many other approaches have also been reported including the reaction of arylmagnesium bromides and 2-aminobenzonitriles[2r,s] or palladium-catalyzed carbonylative Suzuki coupling reaction of 2-iodoanilines with arylboronic acids.[2t–v] We wish to report herein 2-arylindoles as a new entry to 2-aminobenzophenones under transition metal-free conditions without the use of air-sensitive organometallic reagents.



Scheme 1. Synthesis of 2-aminobenzophenones.

Results and Discussion

Recently, an interesting β-arylation of indoles with nitroarenes under aerobic oxidation conditions has been reported by Kumar *et al.*[3] The reaction of 2-methylindole and nitrobenzene in the presence of KO^{t}Bu in DMSO afforded 2-methyl-3-(4-nitrophenyl)indole in moderate yield via an oxidative nucleophilic substitution of hydrogen (ONSH) pathway.[3] In order to prepare 2,3-diarylindole **3** by using the method of Kumar, we examined the reaction of 2-phenylindole (**1a**) and nitrobenzene in DMSO in the presence of KO^{t}Bu under O_2 balloon atmosphere at room temperature. No reaction was observed presumably due to steric hindrance between the phenyl group of **1a** and incoming nitrobenzene moiety. Thus, we examined the reaction at elevated temperature (90 °C), as shown in Scheme 2. The formation of **3** was not observed even at 90 °C;



Scheme 2. Unexpected formation of 2-aminobenzophenone (**2a**).

however, 3-hydroxy-3-phenyl-2-oxindole (**4**)[4] was isolated in good yield (61%) along with a trace amount (4%) of 2-aminobenzophenone (**2a**), unexpectedly. The yield of **2a** was increased to 48% when the reaction was carried out at 140 °C for 6 h. The result stated that compound **4** would be an intermediate for the formation of **2a** (*vide infra*), and the reaction showed similar reactivity in the absence of nitrobenzene.

Encouraged by the result an optimum reaction condition for the synthesis of **2a** was examined, and the results are summarized in Table 1. No reaction was observed in the presence of KO^{t}Bu in DMSO at room temperature (entry 1). The reactions at 90 °C and 140 °C for 8 h (entries 2 and 3) showed similar results to that shown in Scheme 1. The use of Cs_2CO_3 at 90 °C was somewhat sluggish (entry 4); however, the reaction at 140 °C (entry 5) afforded **2a** in good yield (60%). The use of 1.0 equiv of Cs_2CO_3 (entry 6) or DMF as solvent (entry 7) was less effective. The reaction at lower temperature (120 °C, entry 8) and the use of K_2CO_3 (entry 9) were also less effective. The use of KOH at 90 °C (entry 10) afforded **4** in good yield (73%); however, the yield of **2a** was low at 140 °C (entry 11). The reaction under N_2 balloon atmosphere showed almost no reaction.

Under the optimized condition (entry 5 in Table 1) the reactions with various 2-substituted indoles **1b–1o** were examined, and the results are summarized in Table 2. The reactions of 5-chloro-2-phenylindole (**1b**) and 5-methyl-2-phenylindole (**1c**) afforded **2b** and **2c** in reasonable yields (59 and 55%, respectively). Similarly, the corresponding 2-aminobenzophenones **2d–2j** were synthesized in moderate yields (47–60%) from **1d** to **1j**. 2-*tert*-Butylindoles **1k** and **1l** also afforded **2k** and **2l** in moderate yields (58 and 56%, respectively). However, 2-methylindole (**1m**) was decomposed completely under the present reaction conditions. No reactions were observed with indoles **1n** and **1o**, bearing a nitro group.

The mechanism is not clear at this stage; however, we could propose a tentative mechanism, as shown in Scheme 3. 2-Phenylindole (**1a**) was converted to 3-phenyloxindole **VI** via semipinacol type rearrangement of epoxide intermediate **IV**.[5] A subsequent aerobic oxidation of **VI** to 3-hydroxyoxindole **4**[6] and a following oxidative ring-opening furnished **2a**.[7] During the conversion of **4** to **2a**, loss of one carbon atom (2-position of **4**) might occur as reported.[7a,8] As noted above in Scheme 2 and Table 1, the conversion of **1a** to **4** could proceed at 90 °C, while the conversion of **4** to **2a** required somewhat higher reaction temperature (140 °C). No reaction was observed for *N*-methyl-2-phenylindole (**1p**), and the result stated that the formation of indole anion **I** is essential for the reaction. The formation of **4** might also occur via the oxidation of **III** or **IV** to 2-hydroxyindoxyl intermediate **VII**[5d,9] and a subsequent α-ketol rearrangement,[10] as also shown in Scheme 3.

It is interesting to note that the reaction of 2-phenyl-3-methylindole (**1q**) afforded 2-phenyl-4-quinolone (**5**), albeit in low yield (36%), under the same reaction conditions (Cs_2CO_3/DMSO/140 °C/4 h), as shown in Scheme 4. The formation of 3-methyl-3-phenyl-2-oxindole was not observed. Quinolone **5** might be produced via the corresponding hydroperoxide **II'**, dioxetane **VIII**,[5e,11] *N*-(2-ketoaryl)amide **IX**, and the final base-promoted Camps cyclization of **IX**.[12] Such a conversion of 2,3-disubstituted indoles to quinolones has been well known as Witkop–Winterfeldt oxidation.[13]

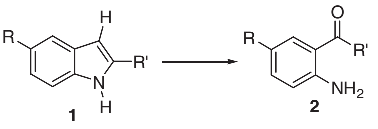
In summary, various 2-aminobenzophenones were synthesized from 2-arylindoles in DMSO under O_2 balloon atmosphere. The synthesis was carried out without the use

Table 1. Optimization of reaction conditions.[a]

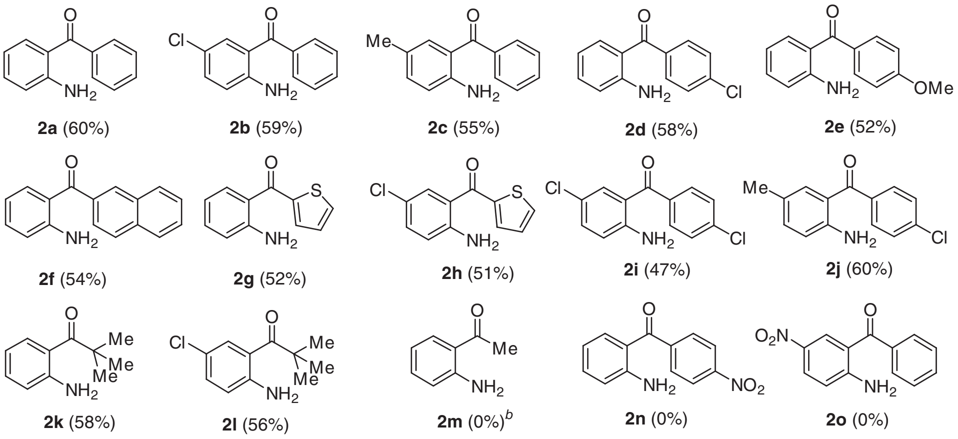
Entry	Conditions	**1a** (%)[b]	**4** (%)	**2a** (%)
1	KO^{t}Bu (2.0 equiv), DMSO, rt, 8 h	<95	<5	0
2	KO^{t}Bu (2.0 equiv), DMSO, 90°C, 8 h	0	64[c]	<5
3	KO^{t}Bu (2.0 equiv), DMSO, 140°C, 8 h	0	<5	52[c]
4	Cs_2CO_3 (2.0 equiv), DMSO, 90°C, 8 h	37[c]	41[c]	<5
5	**Cs_2CO_3 (2.0 equiv), DMSO, 140°C, 8 h**	**0**	**<5**	**60**[c]
6	Cs_2CO_3 (1.0 equiv), DMSO, 140°C, 8 h	0	<10	51[c]
7	Cs_2CO_3 (2.0 equiv), DMF, 140°C, 8 h	0	<10	43[c]
8	Cs_2CO_3 (2.0 equiv), DMSO, 120°C, 8 h	0	<10	52[c]
9	K_2CO_3 (2.0 equiv), DMSO, 140°C, 16 h	67[c]	<10	12[c]
10	KOH (2.0 equiv), DMSO, 90°C, 8 h	0	73[c]	<5
11	KOH (2.0 equiv), DMSO, 140°C, 8 h	0	13[c]	43[c]
12[d]	Cs_2CO_3 (2.0 equiv), DMSO, 140°C, 8 h	>90	0	<5

[a] Conditions: **1a** (0.5 mmol) and O_2 balloon are common in all entries.
[b] Recovered starting material.
[c] Isolated yield.
[d] N_2 balloon atmosphere.

Table 2. Conversion of 2-arylindoles to 2-aminobenzophenones.[a]



1a: R = H, R' = Ph; **1b**: R = Cl, R' = Ph;
1c: R = Me, R' = Ph; **1d**: R = H, R' = 4-chlorophenyl;
1e: R = H, R' = 4-methoxyphenyl; **1f**: R = H, R' = 2-naphthyl;
1g: R = H, R' = 2-thienyl; **1h**: R = Cl, R' = 2-thienyl;
1i: R = Cl, R' = 4-chlorophenyl; **1j**: R = Me, R' = 4-chlorophenyl;
1k: R = H, R' = *tert*-butyl; **1l**: R = Cl, R' = *tert*-butyl;
1m: R = H, R' = Me; **1n**: R = H, R' = 4-nitrophenyl;
1o: R = NO_2, R' = Ph



2a (60%) **2b** (59%) **2c** (55%) **2d** (58%) **2e** (52%)

2f (54%) **2g** (52%) **2h** (51%) **2i** (47%) **2j** (60%)

2k (58%) **2l** (56%) **2m** (0%)[b] **2n** (0%) **2o** (0%)

[a] Conditions: Indole **1** (0.5 mmol), Cs_2CO_3 (1.0 mmol), DMSO, 140 °C, 8 h, O_2 balloon.

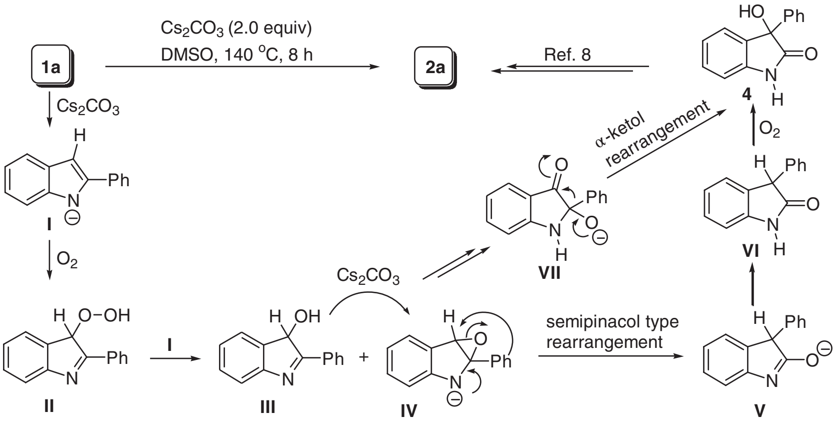
[b] Decomposition was observed.

of a transition metal catalyst or moisture-sensitive organometallic reagents from readily available 2-arylindoles, although the yields were moderate. Further studies on reaction mechanism and substrate scope are under progress.

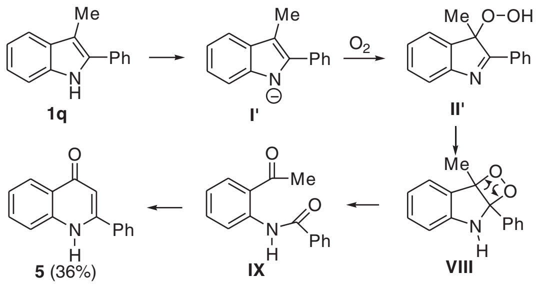
Experimental Section

Typical Procedure for the Synthesis of 2a. A solution of 2-phenylindole (**1a**, 97 mg, 0.5 mmol) and Cs_2CO_3 (326 mg, 1.0 mmol) in DMSO (1.5 mL) was heated to 140 °C for 8 h under O_2 balloon atmosphere. After the usual aqueous extractive workup and column chromatographic purification process (*n*-hexane/Et_2O, 10:1), 2-aminobenzophenone (**2a**) was obtained as a white solid, 59 mg (60%). Other compounds were prepared similarly, and the selected spectroscopic data of **2a–2c** are as follows. All compounds were known,[2] and the structures were confirmed by comparison of their melting points, ^1H and ^{13}C NMR spectra, and mass data with the reported.

2-Aminobenzophenone (2a): 60%; yellow solid, m.p. 108–110 °C (lit.[2o] 111–112 °C); ^1H NMR ($CDCl_3$, 300 MHz) δ 6.09 (s, 2H), 6.60 (t, *J* = 8.4 Hz, 1H), 6.74 (d,



Scheme 3. Proposed mechanism for the convertion **1a** to **2a**.



Scheme 4. Formation of **5** from **1q**.

J = 8.4 Hz, 1H), 7.29 (t, J = 8.4 Hz, 1H), 7.42–7.49 (m, 3H), 7.50–7.56 (m, 1H), 7.61–7.67 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 115.48, 116.96, 118.12, 128.05, 129.09, 131.01, 134.21, 134.57, 140.06, 150.89, 199.07; ESIMS *m*/*z* 198 [M^++H].

2-Amino-5-chlorobenzophenone (2b): 59%; yellow solid, m.p. 94–96 °C (lit.[2o] 97–98 °C); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.08 (s, 2H), 6.69 (d, J = 8.7 Hz, 1H), 7.24 (dd, J = 8.7, 2.7 Hz, 1H), 7.41 (d, J = 2.7 Hz, 1H), 7.44–7.52 (m, 2H), 7.53–7.60 (m, 1H), 7.61–7.67 (m, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 118.43, 118.75, 119.91, 128.29, 129.06, 131.48, 133.21, 134.14, 139.27, 149.33, 197.97; ESIMS *m*/*z* 232 [M^++H], 234 [M^++H + 2].

2-Amino-5-methylbenzophenone (2c): 55%; yellow solid, m.p. 62–64 °C (lit.[2q] 59 °C); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.18 (s, 3H), 5.92 (s, 2H), 6.67 (d, J = 8.4 Hz, 1H), 7.13 (d, J = 8.4 Hz, 1H), 7.23 (s, 1H), 7.42–7.56 (m, 3H), 7.62–7.67 (m, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 20.29, 117.10, 118.20, 124.57, 128.04, 129.09, 130.97, 134.03, 135.36, 140.16, 148.73, 199.03; ESIMS *m*/*z* 212 [M^++H].

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Supporting Information. Additional supporting information is available in the online version of this article.

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8. Actually, compound **4** was converted to **2a** in good yield (75%) under optimized reaction conditions (Cs_2CO_3/DMSO/140 °C/O_2 balloon) in short time (2 h).
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