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Corrigendum

Corrigendum to “Microwave-enhanced and ligand-free copper-catalyzed cyanation of aryl halides with $K_4[Fe(CN)_6]$ in water” [Tetrahedron Lett. 50 (2009) 4595–4597]

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Since the publication of this Letter, the authors were questioned by several chemists who could not reproduce the experimental procedure successfully.

In order to allow the experiment to be easily reproduced, the experimental procedure was revised by the authors and has been described in more detail in the corrigendum below.

As is reported by Leadbeater,[1] the cyanation reaction with water as solvent is highly concentration dependent. In our experiment, it was observed that the volume of the solvent decreased from 2 mL to 0.4–0.9 mL at the end of the reaction, which would cause an increase in the concentration of the reaction system. In order to allow the experiment to be easily reproduced, the experimental procedure was revised as follows: the reaction tube was absolutely sealed by melting the mouth of the tube, and 0.7 mL solvent was used.

Our recent investigation revealed that the temperature control system of our scientific microwave apparatus was less reliable. When the temperature was set at 140 °C, the microwave apparatus showed that the temperature of the reaction system ranged from 133 °C to 148 °C, while the actual temperature of the reaction system ranged from 183 °C to 205 °C (the actual temperature was measured by using a mercury thermometer). So the reaction temperature in our procedure should have been corrected as 183–205 °C.

In addition, the typical procedure for the cyanation of aryl bromides has not been described in our original paper. Therefore, such a procedure is herein supplied.

The authors regret failing to cite a similar prior work.[2] We apologize to the workers concerned for this oversight and are pleased to acknowledge their contributions.

According to the above-mentioned investigation, the experimental procedure was revised and optimized as follows:

Typical procedure for the cyanation of aryl iodide: 0.1 mmol copper salt and 0.7 mL H_2O were added into a 25 mL tube. After the mixture was stirred to give a homogeneous solution, $K_4[Fe(CN)_6]\cdot 3H_2O$ (0.3 mmol) and TBAB (1 mmol) were added. Then the mixture was again stirred until a homogeneous solution was obtained. Next, aryl iodide (1 mmol) was added, the tube was sealed by melting its mouth, and was placed into a tetraglycol bath in the microwave cavity. Subsequently, the mixture was heated to 185 °C and was stirred for 50 min at 185 °C. After the cyanation product was purified by column chromatography, the yield was obtained. The parallel experiment was performed. The product from the two parallel experiments was combined and again purified. The purified product was identified by ^1H NMR and ^{13}C NMR.

Note: By applying the revised procedure, the repeating experiments for cyanation of aryl iodides gave similar results as those given in Table 2 (except entry 11) of our original paper.

Typical procedure for the cyanation of aryl bromide: After 0.15 mmol copper salt and 0.2 mL H_2O were added into a 25 mL tube, the mixture was stirred until the solid was fully dissolved. Subsequently, 0.5 mmol ethylenediamine (according to our original experimental records, DMEDA should have been corrected as ‘ethylenediamine’) was added, and the mixture was stirred for 2 min. Then $K_4[Fe(CN)_6]\cdot 3H_2O$ (0.3 mmol), KI (0.25 or 4 mmol), TBAB (1 mmol), and 0.5 mL H_2O were added. After the mixture was stirred to give a homogeneous solution, aryl bromide (1 mmol) was added. Then the tube was sealed by melting its mouth and was placed into a tetraglycol bath in the microwave cavity. Subsequently, the mixture was heated to 200 °C and was stirred for 50 min at 200–208 °C. The purified product was combined with the same product from aryl iodide and was identified by ^1H NMR and ^{13}C NMR.

Note: Our recent investigation revealed that the KI (chemically pure) used in our work contained trace quantities of Ni compound, which had possibly a significant effect on the KI-accelerated cyanation. In the case of using chemically pure KI, the repeating experiments for cyanation of aryl bromides gave similar results as those given in Table 2 (except entry 28) of our original paper by applying the revised procedure. In the case of using analytically pure KI, the results were obtained as follows (Table 1):

We apologize to the readers for any confusion that these mistakes may have caused. A full account, with experimental details, will be published separately.

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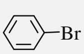
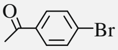
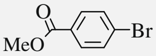
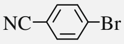
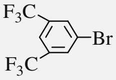
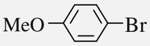
Table 1
KI-accelerated cyanation of bromides catalyzed by $Cu(OAc)_2\cdot H_2O$

Additive	KI (analytically pure) + ethylenediamine					
Substrate						
Yield (%)	48	31	33	21	66	45

References and notes

1. DeBlase, C.; Leadbeater, N. E. *Tetrahedron* **2010**, *66*, 1098–1101.
2. Velmathi, S.; Leadbeater, N. E. *Tetrahedron Lett.* **2008**, *49*, 4693–4694.