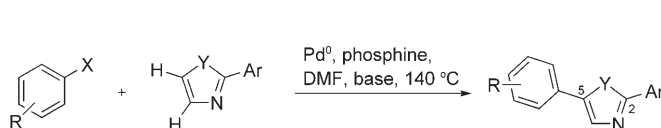


Direct Arylation of Thiazoles on Water**

Gemma L. Turner, James A. Morris, and Michael F. Greaney*

The intermolecular coupling of π -excessive heteroarenes with aryl halides is a principal reaction system in the rapidly growing area of transition-metal-catalyzed direct arylation.^[1,2] The approach contrasts with traditional sp^2 – sp^2 cross-coupling chemistry involving stoichiometric organometallic compounds, such as $ArB(OH)_2$, $ArSnR_3$, $ArZnCl$, as nucleophilic components. In direct arylation, formally unactivated C–H bonds are used as the functionalization site on the nucleophilic coupling partner. Regioselectivity between different C–H bonds is frequently high; in the absence of directing-group effects the 2-substituted heteroarenes shown in Scheme 1 undergo arylation at the most electron-rich 5-position through a postulated S_EAr mechanism.^[3,4]

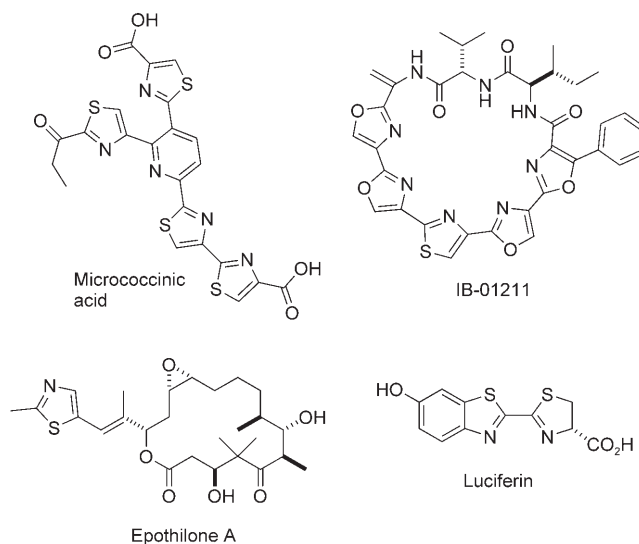


Scheme 1. Generalized intermolecular azole direct arylation. Y = O, S, NR.

Nearly all intermolecular (and many intramolecular) heteroarene direct arylations require harsh reaction conditions in terms of high temperatures and corresponding high-boiling solvents, such as dimethylformamide (DMF). Indeed, the reaction conditions developed by the groups of Ohta and Miura in their pioneering work on heteroarene direct arylations (anhydrous DMF, 140 °C, inorganic base, $Pd(OAc)_2$ plus phosphine ligand)^[3a,5] have become the standard operating procedure, being heavily represented amongst existing reports.^[1,6] Whilst these vigorous conditions may not cause undue difficulty in the functionalization of simple heteroarenes for medicinal chemistry screening programmes, they represent a serious limitation when applied to the synthesis of

more-complex heteroarenes of the type found in natural products. With this in mind, we were interested in developing new ways of conducting heteroarene direct arylation that exemplify mildness and ease-of-use. We report herein our results on the direct arylation of thiazoles, featuring the first direct arylation system that works “on water”.

Arylated and alkenylated thiazoles have vast application, being prominent components of biologically active natural products (Scheme 2) as well as agrochemicals, drug molecules, and novel optical materials. As a result, they have been popular substrates in direct arylation studies.^[3a,7]



Scheme 2. Selected examples of bioactive thiazole-containing natural products.

We were aware at the outset of the report by Mori et al.^[8] on the arylation of 2-anisylthiazole in DMSO under the relatively mild temperature of 60 °C in the presence of AgF , suggesting that there may be scope for developing a more general arylation methodology under mild conditions. We chose to study the arylation of 2-phenylthiazole (**1**) with *p*-chloroiodobenzene (**2a**).^[9] The choice of a less-strongly electron-donating group in the 2-position (compared to anisyl) was made with a view to developing a robust arylation methodology that would have broad applicability.

Initial optimization studies established that the reaction could proceed in the more user-friendly acetonitrile as solvent at 60 °C over 3 days (Table 1), and that the cheaper Ag_2CO_3 could be employed as both silver source and base (2 equiv). The exact role of the silver additive in the reaction mechanism is unclear at this stage, however we note that an inhibitory effect of iodide has been recorded in a number of arylation

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[**] We thank Syngenta and the EPSRC for funding and the EPSRC mass spectrometry service at the University of Swansea. Stephan Ohnmacht is thanked for the preparation of compound **13**.

Supporting information for this article is available on the WWW under <http://www.angewandte.org> or from the author.

Table 1: Arylation of 2-phenylthiazole (**1**).

$\text{Ar-I} + \text{H} \begin{array}{c} \text{S} \\ \diagup \quad \diagdown \\ \text{C} \quad \text{N} \\ \text{H} \end{array} \text{Ph} \xrightarrow[\text{MeCN, 72 h or H}_2\text{O, 24 h}]{[\text{Pd}(\text{dppf})\text{Cl}_2] \cdot \text{CH}_2\text{Cl}_2, \text{PPh}_3, \text{Ag}_2\text{CO}_3, 60^\circ\text{C}}$ $\text{Ar} \begin{array}{c} \text{S} \\ \diagup \quad \diagdown \\ \text{C} \quad \text{N} \\ \text{H} \end{array} \text{Ph}$				
Entry	ArI ^[a] (2)	Product (3)	Yield in MeCN [%] ^[b]	Yield in H ₂ O [%]
1			81	95
2			74	90
3			62	67
4			78	> 99
5			89	> 99
6			65	> 99
7			59	82
8			71	82
9			53	88
10			62	> 99
11			np	> 99
12			65	81
13			0	> 99
14			57	71
15			36	> 99
16			53	> 99
17			0	> 99
18			61	> 99
19 ^[c]			0	56

Table 1: (Continued)

Entry	ArI ^[a] (2)	Product (3)	Yield in MeCN [%] ^[b]	Yield in H ₂ O [%]
20			np	88

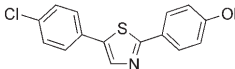
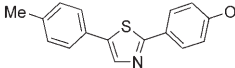
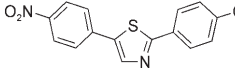
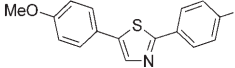
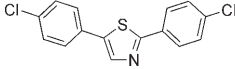
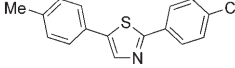
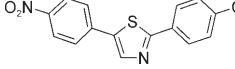
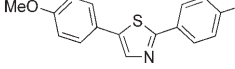
[a] See the Experimental Section for the reaction procedure. [b] np = not performed. [c] anis = 4-methoxyphenyl.

systems mandating the addition of Ag⁺ sequestering agents.^[2c,10] Arylation was entirely unsuccessful in the absence of Ag₂CO₃ under these conditions. We found a combination of [Pd(dppf)Cl₂]·CH₂Cl₂/PPh₃, dppf = (diphenylphosphanyl)-ferrocene) to be an effective catalyst system, although there was good tolerance for a number of Pd salt/ligand combinations. Most importantly, the reaction is successful for a wide variety of electrophiles, effectively arylating **1** with the complete spectrum of aryl iodides. Both electron-rich (R = Me, OMe) and electron-poor (R = F, Cl, CF₃, CN, CO₂Et, COMe, NO₂) reacting partners coupled in generally good yields, with substitution being tolerated at each of the *o*, *m*, and *p*-positions. We were pleased to observe that certain heterocyclic iodides were viable for direct arylation, forming the pyridyl thiazoles **3n** and **3o** and the novel 5–5 linked symmetrical dithiazole **3r**; albeit in moderate yield. The only failures we observed in the system were the hindered mesityl iodide (**2m**) and the heterocyclic pyrazine (**2q**) and thiazole (**2s**) iodides, all of which completely failed to react to give the product. Aryl bromides were less-effective than iodides in every case, and triflates were not viable at all in the reaction.

We next varied the electronics of the thiazole substrate by changing the 2-phenyl substituent, studying the electron-withdrawing *p*-CF₃ (**4b**) group along with the electron-donating *p*-OMe (**4a**) and *p*-Me (**4c**) groups (Table 2 and the Supporting Information). The results are consistent with the S_EAr mechanism commonly put forward for direct arylation of the azole 5-position, with the electron-rich anisyl-substituted thiazole **4a** clearly providing the higher yields of arylation (64–98%) when compared with the electron-poor substrate **4b** (12–74%). The *p*-Me series produces comparable arylation yields (69–85%) to the parent phenyl series (62–81%, entries 1–4 in Table 1). Examining the electrophile, we observe that *p*-nitro-iodobenzene **2c** is somewhat anomalous, producing the lowest yields (**3c**, Table 1, **5c,g**, Table 2; 12–64%). This result is likely due to the high reactivity of this iodide promoting deleterious side-reactions.

The reaction system compares very favorably with existing thiazole arylations,^[7] working in higher yield for a far greater substrate range, embracing polarity differences across electrophile and nucleophile, being considerably milder at *T* = 60 °C, and using a simple and relatively inexpensive catalyst system. With this methodology in hand, we turned our attention to improving the reaction time, which at three days was sub-optimal. Interestingly, our reaction system appears dichotomous with the established Ohta/Miura con-

Table 2: Arylation of 2-aryl thiazoles.

		$\text{Ar}^1\text{-I} + \text{H} \begin{array}{c} \text{S} \\ \diagup \quad \diagdown \\ \text{C} \quad \text{N} \end{array} \text{Ar}^2$		$\xrightarrow[\text{MeCN, 72 h or H}_2\text{O, 24 h}]{[\text{Pd}(\text{dppf})\text{Cl}_2] \cdot \text{CH}_2\text{Cl}_2, \text{PPh}_3, \text{Ag}_2\text{CO}_3, 60^\circ\text{C}}$		$\text{Ar}^1\text{-S} \begin{array}{c} \text{S} \\ \diagup \quad \diagdown \\ \text{C} \quad \text{N} \end{array} \text{Ar}^2$	
2		4a: Ar ² = 4-MeOC ₆ H ₄ 4b: Ar ² = 4-CF ₃ C ₆ H ₄ 4c: Ar ² = 4-MeC ₆ H ₄				5	
Entry	Ar ¹ [^a]	Thiazole substrate[^c]	Thiazole product	Yield in MeCN [%]	Yield in H ₂ O [%] ^[b]		
1	2a	4a		98	np	(5a)	
2	2b	4a		96	np	(5b)	
3	2c	4a		64	91	(5c)	
4	2d	4a		73	np	(5d)	
5	2a	4b		63	> 99	(5e)	
6	2b	4b		32	> 99	(5f)	
7	2c	4b		12	79	(5g)	
8	2d	4b		74	82	(5h)	

[a] See the Experimental Section for the reaction procedure. [b] np = not performed.

[c] See the Supporting Information for the arylation of 4c.

ditions as it did not respond well to increasing temperature; microwave heating of the reaction in excess of 100 °C, for example, lead to extensive homocoupling of the aryl iodide with little if any direct arylation.

A more productive approach was to change the solvent. A screen indicated that direct arylation was viable in each of THF, CHCl₃, dioxane, MeOH, and toluene. We were surprised to find, however, that water gave by far the best results of all—very clean conversions were observed after 24 h at 60 °C, with the arylated products being isolated in high yield. Repeating the arylations of the compounds in Table 1 and Table 2 in water resulted in substantially higher yields in every case. For some substrates, the difference was remarkable. The mesityl thiazole (**3m**, Table 1), which was not formed at all using acetonitrile, was produced in quantitative yield under aqueous conditions. Likewise, synthesis of the bithiazoles **3r** and **3s**, problematic in MeCN, was substantially improved. We extended the aqueous procedure to the novel pyrazine thiazole **3q** (Table 1) and the *p*-bromo compound **3k** (Table 1), featuring a versatile handle for further functionalization through cross-coupling. We also synthesized the 5-(3,4-dimethoxyphenyl)thiazole **3t**, the thio analogue of balsoxin, an oxazole natural product isolated from the plant *A. Balsamifera*.^[11] The average yield using water as solvent was very high—90% across the complete spectrum of aryl iodides used in the study.

Given the lack of solubility of reactants, reagents, and products in water, the system is an example of what Sharpless has termed an “on-water” reaction, whereby the organic components react in a heterogeneous aqueous suspension.^[12,13] The benefits of conducting on-water chemistry can be substantial: increased efficiency and rate (as seen herein), convenient ease of operation, improved safety profile owing to the excellent heat capacity of water, in addition to the benefits of cost and of water as a green solvent. Work-up of the on-water reactions was straightforward, involving simple filtration, extraction, and concentration methods. In a number of cases (for example, thiazoles **3a,b,d,e**, and **j**) the product sublimed out of the aqueous mixture and could be isolated directly, without any extraction, washing, or further purification being necessary (see the Supporting Information).

A detailed examination of the arylation of thiazole **1** with *p*-chloriodobenzene (**2a**) revealed the reaction to be complete in just 6 h at 60 °C with 5 mol % catalyst loading, compared to 72 h for the reaction in MeCN (Figure 1 A). The loading could be dropped to 0.5 mol % without significant penalty, providing product **3a** in an excellent 90% yield after 24 h. Similarly, the equivalency of silver carbonate could be reduced to 0.5 molar equivalents (1 equiv of Ag⁺, 92% after 24 h). The reaction even proceeded to completion at room temperature, but only after a reaction time of 5 days.

The theoretical basis of rate acceleration both in and on water has been the subject of extensive investiga-

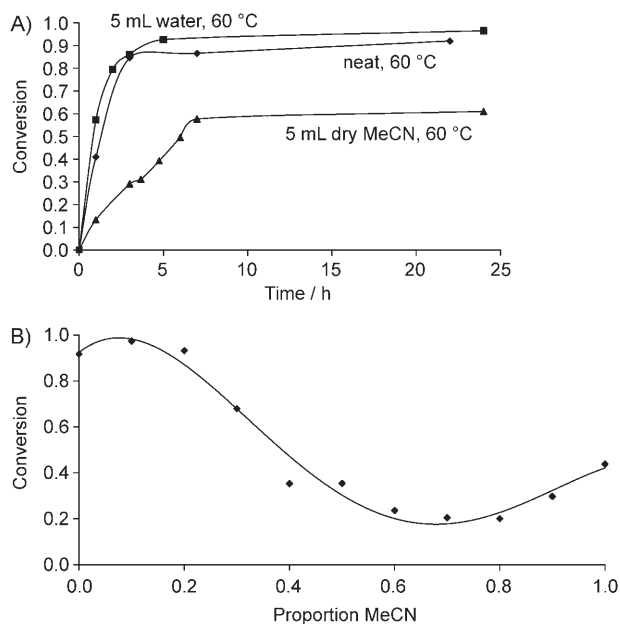
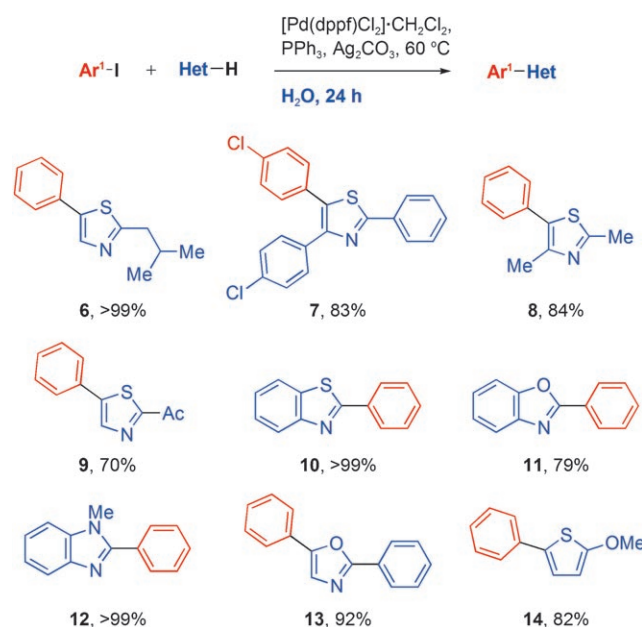


Figure 1. HPLC monitoring of the arylation of **1** with **2a**. A) Conversion over time for three methods. B) Conversion after 24 h in water/MeCN mixtures.

tion.^[14,15] For the system at hand we note that running the reaction neat is nearly as effective as running it on water. This suggests that a substantial increase in the effective concentration of reactants and catalyst system is the main driving force for rate acceleration in an on-water reaction. Examining the relative ratio of water/MeCN in the reaction showed that whilst small amounts of MeCN were well tolerated, increasing the proportion of organic solvent led to a rapid decrease in yield, underlining the requirement for heterogeneity (Figure 1 B). Pending detailed mechanistic investigation, we hold this concentration effect as our principal hypothesis. From the point of view of synthetic expediency, the on-water method is to be recommended over running the reaction neat in all cases, owing to benefits of reproducibility and safety.

Having established high-yielding on-water arylation conditions for 2-aryl thiazoles, we were interested in exploring the scope of the methodology with alternative heterocyclic substrates. Initial results point to a versatile process for high-yielding direct arylation (Scheme 3). 2-Alkyl-substituted



Scheme 3. Direct arylation of five-membered heterocycles on water.

thiazoles were arylated in excellent yield (**6**) along with the more sterically hindered 2,4-disubstituted thiazoles (**7** and **8**) and the versatile 2-acyl thiazole (**9**). Moving away from thiazoles, the three parent benzazole heterocycles were effectively phenylated at the 2-position, with the benzimidazole and benzothiazole affording quantitative yields of product (**12** and **10**). 2-Phenyloxazole and 2-methoxythiophene were likewise efficiently functionalized at the 5-position (**13** and **14**).

In conclusion, we have developed the first direct arylation methodology that takes place on water. The procedure is highly efficient, user-friendly, and has excellent generality, having been applied to the synthesis of heterocycles display-

ing diverse functionalities of relevance to medicinal, materials, and natural products chemistry. In addition, the reaction is carried out under conditions substantially milder than those commonly found in the literature for heteroarene arylation. Future work will look to apply this methodology to the synthesis of complex molecules.

Experimental Section

5-(4-Chlorophenyl)-2-phenylthiazole (3a**):** Representative procedure for cross-coupling in organic solvents: Ag_2CO_3 (342.1 mg, 1.240 mmol, 2 equiv), $[\text{Pd}(\text{dppf})\text{Cl}_2]\cdot\text{CH}_2\text{Cl}_2$ (25.3 mg, 0.031 mmol, 5.0 mol %), PPh_3 (16.3 mg, 0.062 mmol, 10 mol %), 4-chloriodobenzene (177.5 mg, 0.744 mmol, 1.2 equiv), and 2-phenylthiazole (100 mg, 0.620 mmol, 1 equiv) were combined and dissolved in MeCN (5 mL) under N_2 . The reaction was heated at 60 °C for 72 h and filtered through a pad of celite, washed with acetone (5 mL) and CH_2Cl_2 (5 mL), and concentrated under vacuum. The title compound is obtained following purification by column chromatography in 10 % EtOAc/hexane as a colorless solid (136.5 mg, 81 % yield). mp (Et_2O): 137 °C; ^1H NMR (360 MHz, CDCl_3): δ = 7.92 (1 H, s), 7.90–7.87 (2 H, m), 7.47–7.45 (2 H, m), 7.39–7.37 (3 H, m), 7.32–7.30 ppm (2 H, m); ^{13}C NMR (90 MHz, CDCl_3): δ = 167.49, 139.44 (CH), 137.94, 134.10, 133.45, 130.16 (CH), 129.88, 129.28 (2 CH), 128.99 (2 CH), 127.77 (2 CH), 126.36 ppm (2 CH); IR (thin film): $\tilde{\nu}_{\text{max}}$ = 3054, 2986, 1265, 1095, 896, 739, 705 cm^{-1} ; HRMS (ES + ve): calculated for $[\text{C}_{15}\text{H}_{10}^{35}\text{ClNS}+\text{H}]^+$: 272.0295, found: 272.0293.

Representative procedure for cross-coupling on water: Ag_2CO_3 (342.1 mg, 1.240 mmol, 2 equiv), $[\text{Pd}(\text{dppf})\text{Cl}_2]\cdot\text{CH}_2\text{Cl}_2$ (25.3 mg, 0.031 mmol, 5.0 mol %), PPh_3 (16.3 mg, 0.062 mmol, 10 mol %), and 4-chloriodobenzene (177.5 mg, 0.744 mmol, 1.2 equiv) were combined and thoroughly mixed in the bottom of a quickfit testtube. 2-Phenylthiazole (100 mg, 0.620 mmol, 1 equiv) was added, followed by deionized water (5 mL), and the suspension heated to 60 °C for 24 h. The reaction mixture was then filtered through a pad of celite, washing the pad with acetone (10 mL) and CH_2Cl_2 (10 mL), and the organic solvents removed under vacuum. The resultant slurry was partitioned between CH_2Cl_2 (10 mL) and brine (5 mL), and the phases separated. The aqueous phase was extracted with CH_2Cl_2 (10 mL) and the combined organic phases concentrated under vacuum. The crude product was purified by column chromatography in 10 % EtOAc/hexane to afford **3a** as a colorless solid (159.7 mg, 95 % yield).

Representative procedure for cross-coupling neat: Ag_2CO_3 (342.1 mg, 1.240 mmol, 2 equiv), $[\text{Pd}(\text{dppf})\text{Cl}_2]\cdot\text{CH}_2\text{Cl}_2$ (25.3 mg, 0.031 mmol, 5.0 mol %), PPh_3 (16.3 mg, 0.062 mmol, 10 mol %), and 4-chloriodobenzene (295.8 mg, 1.240 mmol, 2 equiv) were combined and shaken to mix thoroughly. 2-Phenylthiazole (100 mg, 0.620 mmol, 1 equiv) was then added and the mixture heated to 60 °C for 24 h. The reaction is a melt for the first several hours but as more product forms it begins to set into a solid cake. CH_2Cl_2 (10 mL) was added to suspend the reaction mixture which was mechanically broken down and filtered through a pad of celite, washed with CH_2Cl_2 (5 mL) and acetone (5 mL), then concentrated under vacuum. The crude product was purified by column chromatography in 10 % EtOAc/hexane to afford **3a** as a colorless solid (162.5 mg, 96 % yield).

Received: May 15, 2007

Revised: July 6, 2007

Published online: September 18, 2007

Keywords: direct arylation · heterocycles · homogeneous catalysis · palladium · water chemistry

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