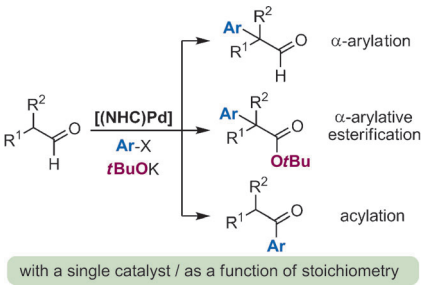
COMMUNICATION

Three′s company: The selective α-arylation and α-arylative esterification of linear and branched aldehydes is reported for a variety of bromoarenes. The acylation of aryl bromides can be achieved with linear aldehydes (see scheme). All these transformations were performed with a single [(N-heterocyclic carbene)Pd] catalyst through adjustment of the stoichiometry of the reagents and the appropriate base.



Cross-Coupling Reactions

*Pradeep Nareddy, Clément Mazet** ____ ▮▮▮▮–▮▮▮▮

α-Arylation, α-Arylative Esterification, or Acylation: A Stoichiometry-Dependent Trichotomy in the Pd-Catalyzed Cross-Coupling between Aldehydes and Aryl Bromides

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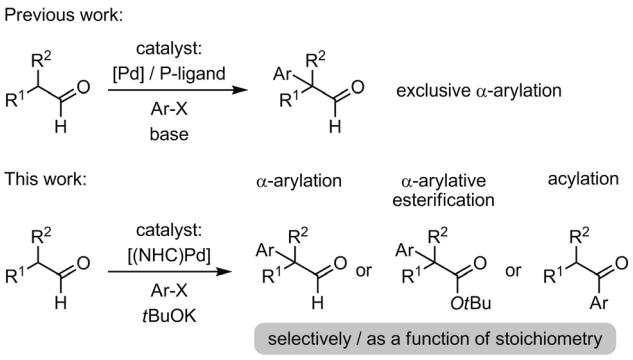
α-Arylation, α-Arylative Esterification, or Acylation: A Stoichiometry-Dependent Trichotomy in the Pd-Catalyzed Cross-Coupling between Aldehydes and Aryl Bromides

Pradeep Nareddy and Clément Mazet*[a]

As a clear testimony of its high synthetic potential, the Pd-catalyzed α-arylation of enolates has attracted increased interest over the last two decades.[1] Although the inherent problems associated with any cross-coupling reaction using aryl halides should not be neglected, taming the reactivity of the carbonyl functionality under the necessary basic conditions certainly constitutes the key challenge of these α-arylations.[1c,f] Therefore, not surprisingly, there exists a plethora of examples with robust carbonyl functions such as amides, esters, or ketones in which the optimized catalyst enables the coupling reaction to proceed with a wide scope of aryl halides and tolerates various functional groups. In contrast, the number of efficient methods for the more sensitive aldehyde functionality is rather limited. Whereas the tendency of these derivatives to undergo self-aldol condensation under basic reaction conditions is the first barrier to overcome, the marked reactivity difference between linear and α-branched substrates constitutes another notorious difficulty. Building on the early observations of Muratake et al. in the syntheses of hesitine-type aconite alkaloids,[2] the Miura, Buchwald, and Hartwig groups have developed protocols that addressed most of these issues.[3–6] Thus, in the best cases, both linear and α-branched aldehydes could be coupled with electron-rich, electron-deficient, or sterically demanding aryl bromides and chlorides. Nonetheless, all these methods require the use of air-sensitive and rather expensive phosphine ligands, which might limit their widespread application.

At the outset of our investigations, we initially aimed at developing a more practical protocol that would rely on the use of air-stable Pd complexes supported by commercially available N-heterocyclic carbene ligands (NHC). In addition to their robustness, such systems are structurally highly modular and enable fine-tuning of the electronic and steric requirements associated with α-arylation processes. Indeed, by following the impetus provided by Hartwig and co-workers,[7] several research groups have utilized [(NHC)Pd] complexes for the α-arylation of amides or ketones.[8,9] Nonetheless, no example of such catalyst was reported for the α-arylation of the more sensitive aldehydes.[10] Herein, we report first the successful development of the α-arylation of linear and α-branched aldehydes by using a well-defined [(NHC)Pd] complex. Second, and more importantly, we disclose the discovery of an unexpected arylative esterification of α-branched aldehydes and of an equally unexpected intermolecular acylation of aryl bromides by simple adjustment of the relative stoichiometry of the coupling partners and the base by using the very same palladium catalyst (Scheme 1).



Scheme 1. Pd-catalyzed α-arylation of aldehydes and competing processes.

The versatile reactivity of NHC salts with aldehydes prompted us to use well-defined palladium complexes rather than in situ protocols to avoid undesired reactions to occur.[11] Thus, **3a** and **3b** were initially selected and engaged in the cross-coupling of octanal **1a** with 4-(*tert*-butyl)bromobenzene **2a** in 1,4-dioxane at 80 °C using *t*BuOK as a base (Table 1).[12,13] When an equimolar amount of these three components was reacted in the presence of 5 mol % of **3a**, the product of self-aldol condensation **4a** was observed exclusively. When the same reaction was carried out with **3b** instead (5 mol %), a barely separable mixture of aldol condensation product **4a** and α-arylation product **5aa** (30:70) was obtained. After gradual optimization, it was found that a 1:2:2 ratio between **1a**, **2a**, and *t*BuOK was the optimal stoichiometry, delivering **5aa** in 52 % yield after purification. By performing the reaction at 100 °C, the α-arylation prod-

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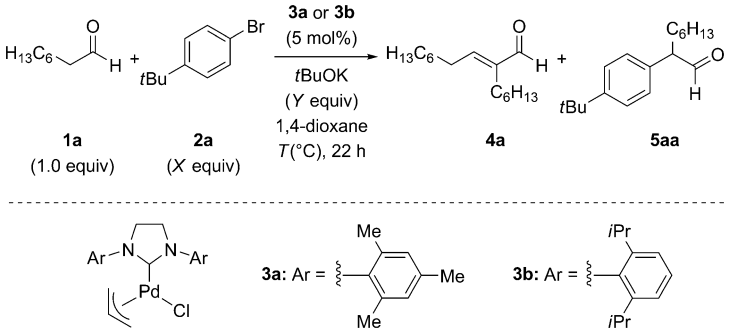
Table 1. Optimization study.[a]



Entry	[Pd]	**2a** (*X* [equiv])	*t*BuOK (*Y* [equiv])	*T* [°C]	Conv [%][b]	**4a**/**5aa**[c]	**5aa** Yield [%][d]
1	**3a**	1.0	1.0	80	>99	>99:1	nd[e]
2	**3b**	1.0	1.0	80	>99	30:70	nd
3	**3b**	2.0	1.0	80	>99	nd[f]	nd
4	**3b**	2.0	2.0	80	>99	12:88	52
5	**3b**	2.0	2.0	100	>99	1:99	68

[a] Average of at least two experiments: **1a** (0.5 mmol). [b] Refers to consumption of **1a**. [c] Determined by ^{1}H NMR spectroscopy. [d] Isolated yield after column chromatography. [e] Not determined. [f] Complex mixture.

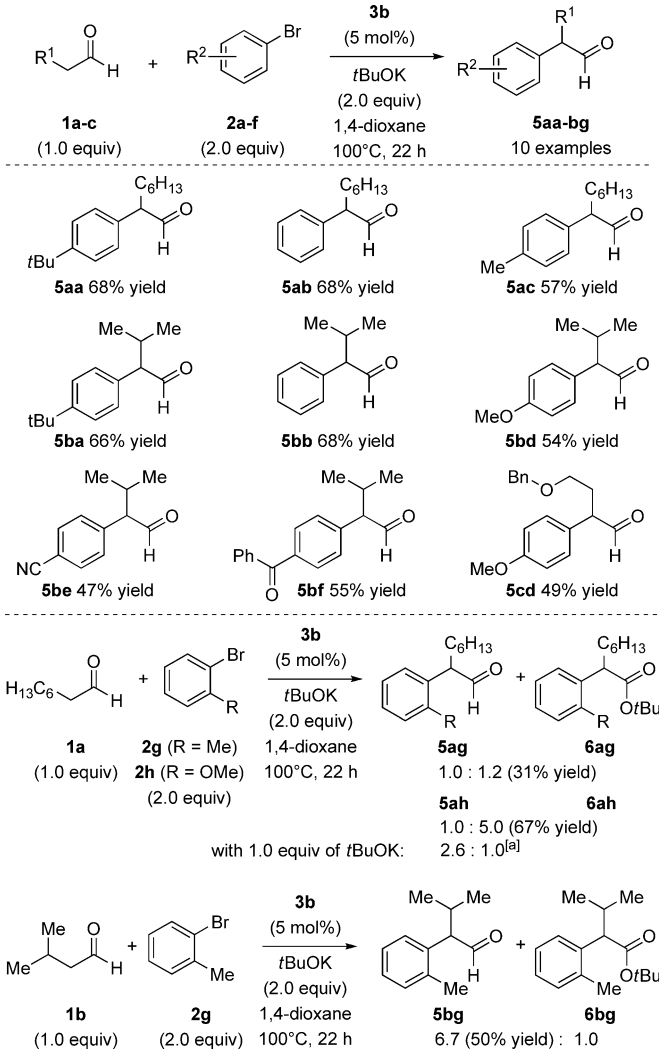
uct **5aa** could be generated exclusively and isolated in 68% yield.

Next, the scope of the intermolecular α-arylation of linear aldehydes was investigated by using this set of reaction conditions (Scheme 2). Gratifyingly, both linear and β-branched aldehydes **1a–c** could be coupled indifferently with electron-rich or electron-neutral aryl bromides (**2a–d**), delivering the corresponding products in 49 to 68% yield after purification by column chromatography. Electron-deficient aryl bromides such as **2e**,**f** were also tolerated, although the yield of the α-arylation products was slightly diminished (47–55%). When **1a** was engaged in the cross-coupling reaction with either 2-bromotoluene **1g** or 2-bromoanisole **2h**, mixtures of the expected α-arylated aldehyde **5ag–h** and the corresponding α-arylated *tert*-butyl ester **6ag–h** were obtained (in reaction with either 2-bromotoluene **1g** or 2-bromoanisole **2h**; ratios of 1:1.2 and 1:5, respectively). The arylated esters could be isolated in 31 and 67% yield, respectively. On the basis of this result, we propose that the intermolecular α-arylation takes place before esterification. Indeed, when only 1 equivalent of base was used, **5ah** was obtained as the major product. The much higher ratio measured in the coupling between **1a** and **2h** suggests that the *ortho*-methoxy substituent might serve as a directing group and facilitate intramolecular C–H activation of the aldehydic proton. Interestingly, Martin and co-workers have recently observed a similar esterification reaction in the Pd-catalyzed intramolecular acylation of aryl bromides when the reaction was carried out in the presence of methanol or *n*-butanol.[14] Similarly, Wu and co-workers have developed an esterification-hydroarylation of alkynylbenzaldehydes with aryl iodides in methanol.[15] In the present study, coupling between two sterically demanding partners such as **1b** and **2g** predominantly led to the formation of the α-arylation product **5bg**.

When our optimized set of reaction conditions was used for the α-arylation of α-branched aldehydes with **1d** and **2a** as model substrates, the corresponding α-arylated *tert*-butyl ester **6da** was obtained exclusively.[16,17] No traces of the initially expected α-arylated aldehyde were detectable by inspection of the crude reaction mixture. The product was isolated in 64% yield after purification by chromatography. Intrigued by this result, we first set out to delineate the scope of this transformation (Scheme 3). Electron-neutral and electron-rich *para*-substituted aryl bromides were particularly well suited, and the corresponding esters with a α-quaternary center were all obtained in good yields (4 examples, 61–77% yield). 4-Fluorobromobenzene could also be coupled, although the corresponding product was obtained in a lower yield (**6di**, 47%). Interestingly, when 2-bromoanisole **2h** was used, a 1:2 mixture of α-arylated ester **6dh** and α-arylated aldehyde **7dh** was obtained, thus indicating that our initial targets might still be accessible. Prior to going in this direction, we sought to gain preliminary insight into the role of the palladium catalyst by performing a series of control experiments (Table 2).

To this end, **7da**, an α-aryl aldehyde bearing a quaternary center, was prepared by using an independent procedure.[4] When first treated with 2 equiv of *t*BuOK in 1,4-dioxane at 100°C, **7da** was found to disproportionate in a 1:1 mixture of the corresponding ester **6da** and alcohol **8da** in a Cannizzaro-type reaction (Table 2, entry 1). Next, when **7da** was treated with 1 equivalent of *t*BuOK in the presence of 5 mol% of **3b**, a 5:1 ratio of **6da**/**8da** was measured. When 2 equivalents of base were employed, this ratio decreased to 2:1, clearly indicating that the Pd-catalyzed esterification and the base-assisted disproportionation reaction are competing processes (Table 2, entries 2 and 3). Of note, in most α-arylative esterifications, we did not measure significant amounts of the alcohols in the crude mixtures. Attempts to perform the α-arylation of ester **6e** proved unsuccessful (Scheme 4). Collectively, the results reported in Table 2 and Scheme 3 suggest that α-arylation likely precedes esterification. This is in line with the observation described in Scheme 2.

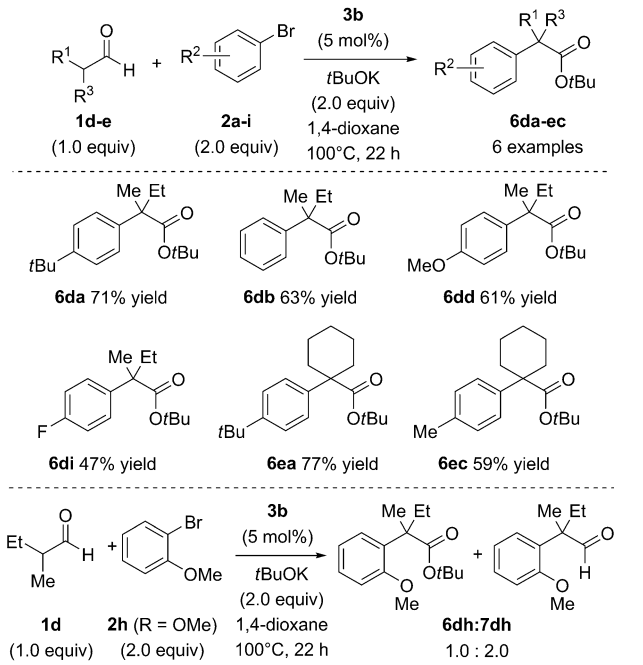
We next searched for reaction conditions that favor the direct α-arylation of α-branched aldehydes (**1d–f**). Gratifyingly, by simply decreasing the relative stoichiometry of *t*BuOK to 1 equivalent, **7da** was obtained exclusively as judged by analysis of the crude reaction mixture and could



Scheme 2. Scope for the α-arylation of linear aldehydes. [a] Along with 7% of **4a**.

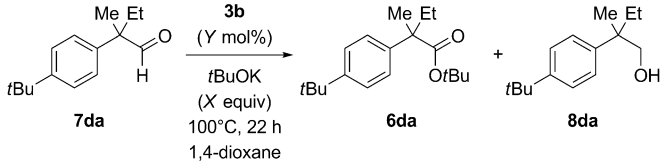
be isolated in 61% yield (Scheme 5). This protocol turned out to be relatively general and was extended to a vast array of bromoarenes that lead to aldehydes with a α-quaternary center. Electron-neutral and electron-rich aryl bromides proved particularly well suited, and the coupling products were isolated in yields that ranged from 47 to 63% (**7da–d**, **7ea**, **7ed**). Sterically demanding *ortho*-substituted electrophiles delivered the product in moderate to good yields (44–72%; **7dg**, **7dj**, **7ek**). Slightly reduced yields were obtained when electron-poor bromoarenes were employed (39–53%; **7de**, **7ee**, **7ei**). Remarkably, even 2-phenylpropanal underwent α-arylation with **2a**, and the formally doubly arylated aldehyde **7fa** was obtained as the sole detectable coupling product (albeit in a modest 31% yield).

During our initial optimization studies, we found that if an excess amount of *t*BuOK (5.5 equiv) were used in the equimolar coupling between **1a** and **2a**, the α-arylation product **5aa** was obtained along with the acylation product **9aa** in a 1:2.3 ratio (Scheme 6).



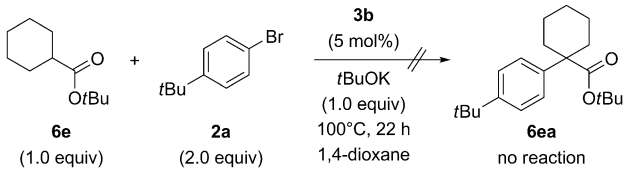
Scheme 3. Scope of the α-arylative esterification of α-branched aldehydes.

Table 2. Control experiments for the arylative esterification.[a]



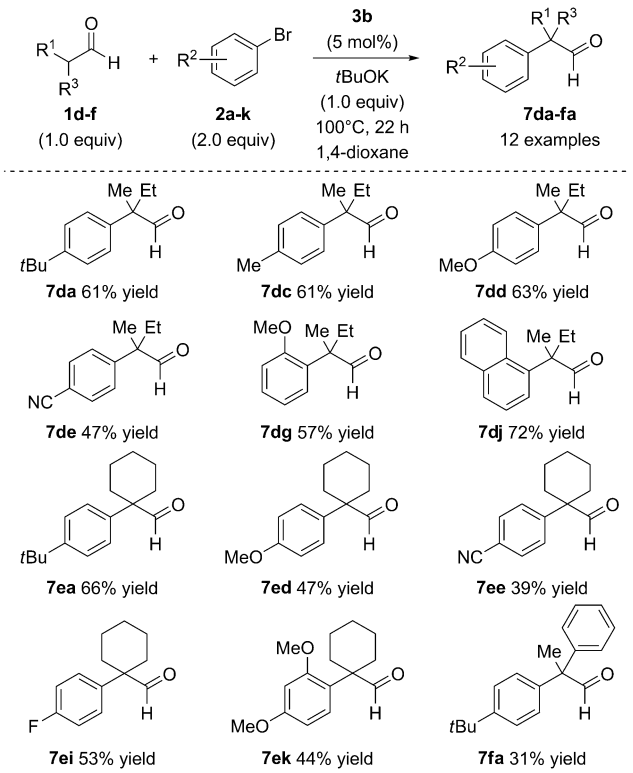
Entry	*t*BuOK (*X* [equiv])	**3b** (*Y* [mol%])	Conv [%][b,c]	**6da/8da**[c]
1	2.0	0	>99	1.0:1.0
2	1.0	5	>99	5.0:1.0
3	2.0	5	>99	2.0:1.0

[a] Average of at least two experiments: **7da** (0.5 mmol). [b] Refers to consumption of **7da**. [c] Determined by ^{1}H NMR spectroscopy.

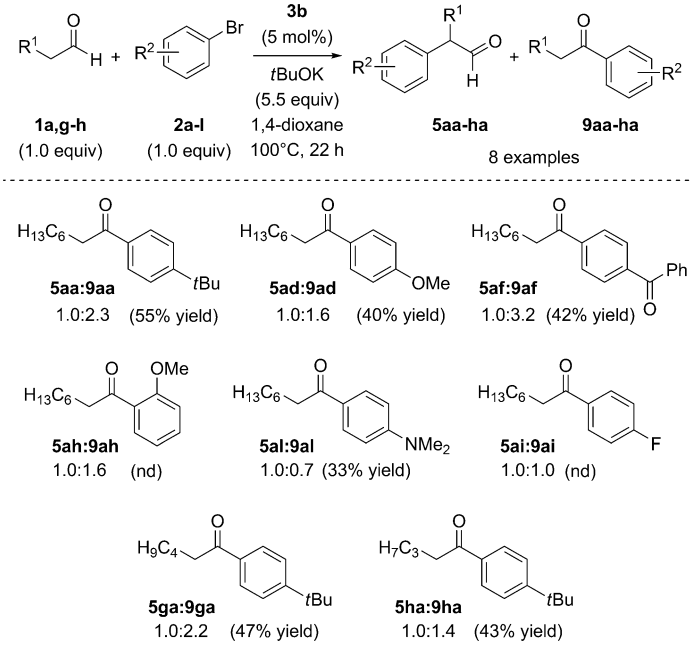


Scheme 4. Unsuccessful α-arylation of α-branched ester **6e**.

Traces of self-aldol condensation or α-arylative esterification were hardly detectable in the crude mixture, and the ketone derivative **9aa** was isolated in 55% after chromatography. This Pd-catalyzed direct acylation reaction is recognized as a challenging process with only a few precedents in the literature.[18–20] We therefore sought to evaluate the scope of this transformation. The process turned out to be applicable to electron-rich, electron-neutral, and electron-



Scheme 5. Scope of the α-arylation of α-branched aldehydes.



Scheme 6. Scope of the acylation of aryl bromides with linear aldehydes.

poor bromoarenes. The ratio between α-arylation and acylation varied between 1.0:0.7 to 1.0:3.2. The presence of the α-arylated aldehyde often complicated the purification procedures, and the acylation products were isolated in yields that ranged from 31 to 55%. When 2-bromoanisole **2g** or 4-fluorobromobenzene **2i** was used, inseparable mixtures of α-arylation and acylation products were obtained. Reactions with α- and β-branched aldehydes delivered complex mixtures that were composed predominantly of α-arylated esters and α-arylated aldehydes.

In conclusion, we have developed a practical protocol for the α-arylation of linear and α-branched aldehydes by using an air-stable and commercially available [(NHC)Pd] complex. We also disclosed a less-common α-arylative esterification of α-branched aldehydes and an unusual acylation of aryl bromides with linear aldehydes by using the very same catalyst. The reasons behind this mechanistic trichotomy are not yet clear, and it is certainly premature to draw any definitive mechanistic hypotheses. Yet it is remarkable that only subtle changes in stoichiometry have such a profound impact on the reaction outcome. In general, similar drastic differences in reactivity are usually observed after modification of the catalyst structure, and/or the reaction temperature or the use of additives.[14,21–23] Current efforts are now directed towards deciphering the key mechanistic aspects of these stoichiometry-dependent transformations.

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Keywords: acylation · arylation · cross-coupling · esterification · palladium

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