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Transition-metal-free Matsuda-Heck type cross-coupling and mechanistic evidence for a radical mechanism.

Julien Bergès,[a] Yassir Zaïd, [a] Anis Tlili,[b] Jean-Marc Sotiropoulos, [c] Marc Taillefer*[a]

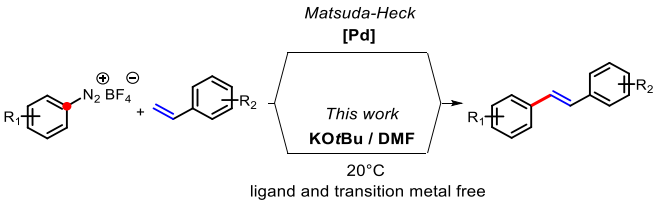
[a] Dr J. Bergès, Dr M. Taillefer
ICGM, Univ Montpellier, CNRS, ENSCM, 34296 Montpellier, France
E-mail: marc.taillefer@enscm.fr
[b] Dr A. Tlili,
Univ Lyon, Université Lyon 1, Institute of Chemistry and Biochemistry (ICBMS – UMR CNRS 5246), CNRS, INSA, CPE-Lyon
1 Rue victor Grignard, F-69622 Villeurbanne (France)
[c] Dr. J.-M. Sotiropoulos
Universite de Pau et des Pays de l'Adour, E2S UPPA, CNRS, IPREM, Pau, France

Abstract: The Matsuda-Heck reaction, usually performed with palladium catalysts, can be carried out under transition metal free conditions in the presence of a KO*t*Bu / DMF couple. This system allows, under mild temperature conditions (20 °C), the selective and direct synthesis of stilbenes from aryldiazonium salts. Mechanistic studies suggest a radical pathway in which the DMF acts as the initiator of the overall process.

Herein, we present a new way to perform the traditionally palladium catalysed Matsuda-Heck reaction under both ligand and transition metal free conditions (Scheme 1).[1,2,3] The latter is a versatile method allowing the preparation of stilbene derivatives by selective alkene functionalization from arenediazonium salts, which constitute highly attractive aryl halide surrogates. Arenediazonium salts are easily prepared from widely available and inexpensive anilines, are often reactive under mild conditions, and the leaving group is inert (N_2) towards the reaction mixture.[4-7] The use of alkenes as starting materials, some of the most widespread chemical compounds, is another advantage of the method. However, the presence of palladium based catalysts for most Matsuda-Heck reactions is not favourable, owing to the high cost and toxicity issues, and limits the attractiveness for large-scale or industrial applications. For the Matsuda-Heck process, the $C_{(sp2)}$-$C_{(sp2)}$ bond formation proceeds via the intermediate formation of a reactive cationic palladium intermediate resulting from the initial oxidative addition of $Pd^{(0)}$ at the $C_{(sp2)}$-N bond of the arenediazonium salts.[3,8] This carbon-carbon bond formation can also be achieved by the Meerwein reaction, a long known copper-mediated coupling between aryldiazoniums and electron-deficient alkenes.[9,10] The method, which suffers from several drawbacks that have limited its application in synthesis, proceeds via reversible oxidation of copper(I) to copper(II), associated to the initial formation of an aryl radical.[11-13] The generation of the latter from arenediazonium has also been performed with an excess amount of iron [14-17] or titanium salts,[18,19] without transition metals [20-24] or through visible-light induced photoredox strategies, often catalyzed by Eosin Y or ruthenium complexes ($Ru(bpy)_3Cl_2$).[25-29] However, with these methods, when the generated aryl radical couples with an alkene, the double bond is often not conserved, which constitutes a great challenge.

We previously discovered that the *α*-arylation of enolizable ketones, usually performed with nickel, palladium or copper catalysts, could be carried out using a simple KO*t*Bu/DMF system that is able to generate aryl radicals in the initiation process.[30f-i] Taking into account the well-known possibility of forming aryl radicals from arene diazonium salts,[4] we assumed that the Matsuda-Heck process could be performed with this system to give stilbenes, which are very important intermediates and targets in the chemical, pharmaceutical, and materials industries.[31]

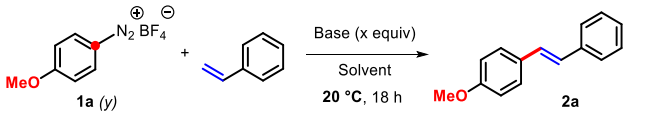
We report herein that a KO*t*Bu/DMF couple alone promotes the direct and selective synthesis of stilbenes by a Matsuda-Heck type-cross-coupling, performed in the absence of ligand and palladium catalyst. We also propose a radical mechanistic pathway based on the literature, alongside experimental and theoretical studies (Scheme 1).



Scheme 1. The Matsuda-Heck reaction: traditional method with palladium catalysts and pathway described herein with KOtBu/DMF system.

To start our investigations, we reacted 4-methoxybenzenediazonium tetrafluoroborate **1a** with styrene in DMF (2 mL) for 18 h at 20 °C in the presence of 2 equivalents of KO*t*Bu. In these conditions, the desired stilbene **2a** (*trans* isomer) was selectively obtained in 39% yield (Table 1, entry 2). Using other bases such as KOAc or NaO*t*Bu gave only traces of **2a** (Table 1, entries 3, 4) and replacing the solvent with acetonitrile, toluene or 1,2-dichoroethane also led to negligible amounts of product (Table 1, entries 5–7). While increasing the amount of KO*t*Bu was moderately beneficial, we noticed the crucial role of the concentration since reducing the volume of DMF to 220 μL and 500 μL afforded **2a** in 45 % and 71 % yields respectively (Table 1, entries 9, 10). Finally, we obtained a very good yield of stilbene **2a** using resublimed KO*t*Bu (purchased from Alfa Aesar - 99.994%), thus ruling out the possibility of a reaction catalyzed by undesirable metallic contaminants (table 1, entry 11).

Table 1. Synthesis of stilbene **2a** from 4-methoxybenzenediazonium tetrafluoroborate **1a** and styrene: reaction conditions.[a]

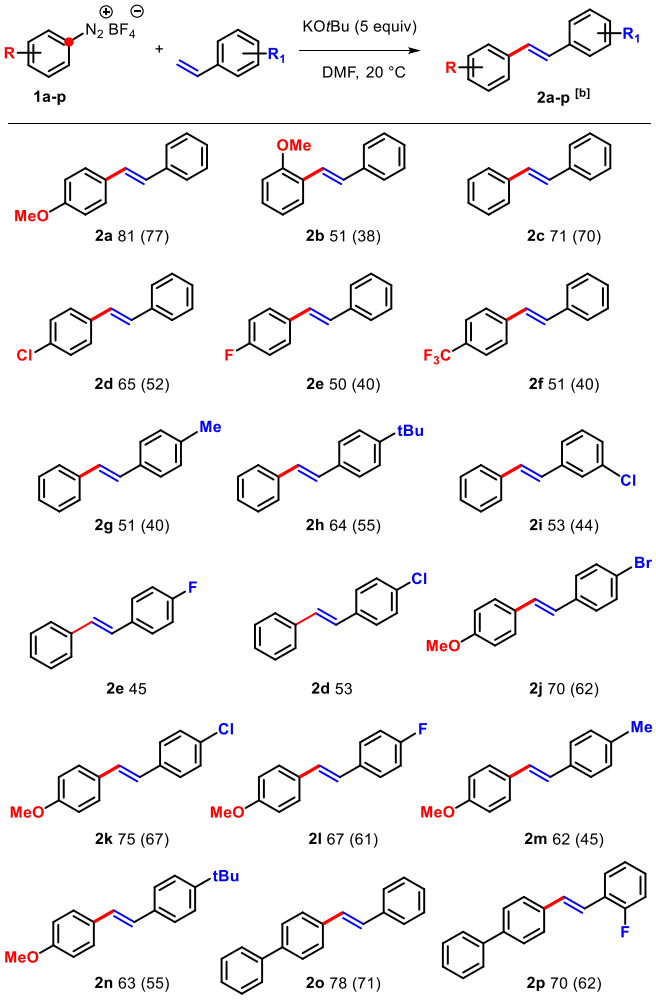


Entry	Base	x	Solvent	y (M)[b]	Yield of **2a** (%)[c]
1	KO*t*Bu	0	DMF	0.5	0
2	KO*t*Bu	2	DMF	0.5	39
3	KOAc	2	DMF	0.5	traces
4	NaO*t*Bu	2	DMF	0.5	< 5
5	KO*t*Bu	2	MeCN	0.5	traces
6	KO*t*Bu	2	Toluene	0.5	0
7	KO*t*Bu	2	DCE	0.5	0
8	KO*t*Bu	5	DMF	0.5	52
9	KO*t*Bu	5	DMF	0.055	45
10	KO*t*Bu	5	DMF	0.125	71 (77[d])
11	KO*t*Bu	5	DMF	0.125	81[d],[e]
12	KO*t*Bu	5	DMF	0.125	0[f]

[a] Reaction conditions: 4-methoxybenzenediazonium tetrafluoroborate **1a** (1 mmol), styrene (2 mmol), base (x mmol), solvent, 18 h at **20 °C**. [b] Molar concentration of **1a** (mol/L). [c] Yields calculated by GCMS using 1,3,5-trimethoxybenzene as an internal standard. [d] 48 h at 20 °C. [e] reaction reformed with resublimed KO*t*Bu purchased form Alfa Aesar (99.994%). [f] Reaction performed with 1.0 equivalent of Galvinoxyl or TEMPO.

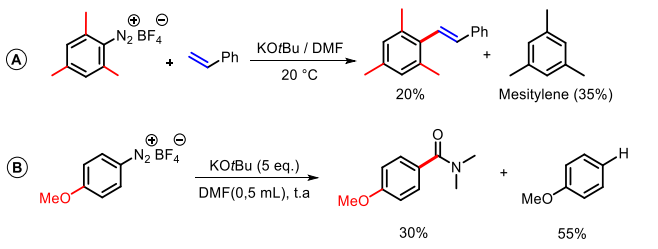
We next explored the scope of the method (Table 2). With the styrene as a coupling partner, the 4-methoxy and the challenging hindered *2*-methoxybenzenediazonium tetrafluoroborates lead to the expected stilbenes **2a** and **2b**. Arenediazonium salts bearing an atom of fluorine or chlorine in the *para* position also produced the corresponding stilbenes (**2d**, **2e**) while in the case of *p*-bromo and *p*-iodo substituents, the reduction of the starting salts to benzene is mainly observed. The benzenediazonium tetrafluoroborate forms the stilbene **2c** and the electron-poor *p*-trifluoromethylbenzene diazonium salt provides the stilbene **2f**, which is an important intermediate in the pharmaceutical industry.[31] This procedure is also compatible with a range of styrene derivatives. Thus the benzenediazonium in the presence of styrenes bearing alkyl substituents (4-Me, 4-*t*Bu) gives the stilbenes **2g** and **2h** respectively, while the *meta*-substituted 3-chlorostyrene leads to the expected coupling product **2i**. The use of benzene- or *p*-anisyldiazonium tetrafluoroborates (**1a**) with other halogenated styrenes (4-Br, 4-Cl, 4-F) as coupling partners also produced the corresponding stilbenes (**2j**-**2l**). The salt **1a** was a suitable substrate for styrenes with electron donating alkyl groups (4-Me, 4-*t*Bu) in the *para* positions, whilst comparatively the electron-poor 4-cyanostyrene resulted in a poor yield (15 mol %). Finally, when the biphenyldiazonium tetrafluoroborate was tested for coupling with styrene and 2-fluorostyrene, the stilbenes **2o** and **2p** were obtained respectively, both in good yields.

Table *2.* Synthesis of stilbenes **2a-p** (*trans* isomers) from styrenes and arenediazonium tetrafluoroborate derivatives: scope of the method.[a]



[a] Reaction performed with 1.0 mmol of arenediazonium tetrafluoroborate, 2 mmol of styrene derivative, 5 mmol of KO*t*Bu in 500µL of DMF, 48 h at 20 °C under argon. [b] NMR yield calculated with 1,3,5 trimethoxybenzene internal as standard. Isolated yield in bracket.

We then turned our attention to the mechanism of this method. As we assumed the reaction to proceed via radical intermediates, we attempted the reactions in the presence of one equivalent of (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) or Galvinoxyl and observed with these common radical scavengers that the coupling of **1a** with styrene was completely inhibited (Table 1, entry 12). Furthermore, repeating the reaction with limited exposure to light resulted in the formation of the coupling product in good yield (77 % of **2a**), thus showing that the reaction is self-generated by the *t*-BuOK/DMF system without assistance from outside light. It should be also noted that for all starting diazonium salts used, the formation of any regioisomers was never observed. The functionalization on the *ipso* position is only obtained, which is inconsistent with the formation of benzyne intermediates and not in agreement with an arynic mechanism. We could also rule out this possibility by carrying out a test from styrene and 2,4,6-trimethylbenzenediazonium tetrafluoroborate which, because of its structure, cannot give rise to reactions proceeding via an aryne intermediate.[32] Under standard conditions we observed, although in low yield, the formation of the expected coupling product (20%) together with the formation of the mesitylene due to the reduction of the corresponding arenediazonium (Scheme 2, **A**).



Scheme 2. A) Reaction of 2,4,6-trimethylbenzenediazonium tetrafluoroborate with styrene. **B**) Evolution of 4-methoxybenzenediazonium tetrafluoroborate in standard conditions.

On the basis of these observations we postulated a radical mechanism, illustrated with the benzenediazonium tetrafluoroborate **1c** (Figure 1).

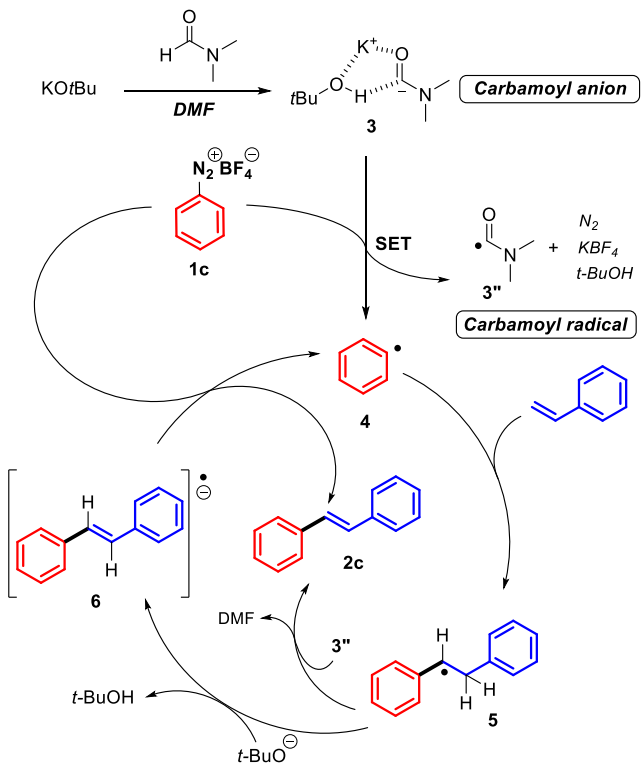


Figure 1. Proposed radical mechanism for the Matsuda-Heck reaction promoted by the KO*t*Bu/DMF system.

The overall process would be initiated by deprotonation of the solvent with KO*t*Bu resulting in the *in situ* formation of the electron-rich carbamoyl anion **3**, stabilized by an interaction with *tert*-butanol and the associated potassium cation. In similar reaction conditions we had previously shown the possibility for this electron-donor active carbamoyl anion to transfer an electron to an aryliodane to form an aryl radical.[30h,32] Taking into account the well-known possibility of generating the latter from arene diazonium salts,[4] we hypothesized that such a development is also possible in the present study. The mechanism would thus, in the presence of diazonium salt **1c** and the carbamoyl anion **3**, lead to the phenyl radical **4** while releasing N_2, KBF_4, *t*-BuOH into the reaction medium, and the corresponding carbamoyl radical **3"**. Propagation could then follow an $S_{RN}1$ pathway in which the phenyl radical **4** reacts with the styrene, thus leading to a new radical intermediate **5**. The tert-butoxide anion then abstracts a proton from the latter, which evolves to the formation of a new radical anion **6**. A final SET from **6** to the starting phenyldiazonium tetrafluoroborate **1c** releases the expected stilbene **2c**. Another possibly would involve the abstraction of a hydrogen radical from **5** by **3"**, with the formation after radical combination of the corresponding stilbene.

In order to assess these hypothesis the process simulation was performed (density functional theory calculations at the M06-2X/6-311+G(d,p) level of theory, the solvent can be taking into account using the polarizable continuum model PCM)(see Figure 2 and the Supporting Information).

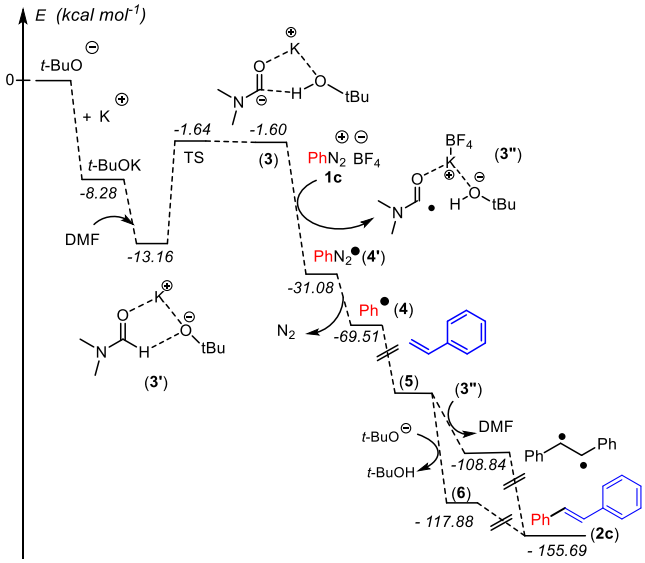


Figure 2. Energie levels (ΔG) for all steps of the reaction starting from the ethanolate. M06-2X/6-311+G(d,p) level of theory, in DMF, is used. ΔG values are given in Kcal.mol^{-1}.

From computed DFT calculations we propose in a first step the formation of a relatively stable complex **3'** (ΔG = - 13.16 kcal mol^{-1}) resulting from the interaction of DMF with KO*t*Bu.[30h] From the latter the anionic carbamoyl adduct **3** would be formed with a quite low activation barrier (ΔG_a = 11.52 kcal mol^{-1}), following the abstraction of a DMF proton by potassium *tert*-butoxide. The corresponding computed transition state is located at an energy level almost similar to that of the anionic carbamoyl **3.** Subsequently, in the presence of the diazonium salt **1c**, an electron transfer would lead to the diazo radical (**4'** ; ΔG = - 29.48 kcal mol^{-1}) which spontaneously decomposes into the phenyl one (**4**). The carbamoyl radical **3"** formed in this step is thermodynamically favorably stabilized by interactions with KBF_4 and *t*-BuOH. DFT calculations then show that the reaction between the generated phenyl radical **4** and the styrene is thermodynamically favorable (ΔG = - 33.05 kcal mol^{-1}) and produces the radical **5**. In the presence of an excess amount of *tert*-butoxide, the passage through an anion radical (**6**) is quite conceivable, the reaction being undeniably controlled by the high thermodynamics towards the corresponding ethylenic **2c** (ΔG = - 37.81 kcal mol^{-1} compared to **6**). The formation of the stilbene via abstraction of a hydrogen radical from **5** by **3"** (ΔG = - 6.28 kcal mol^{-1} compared to **5**) and subsequent formation of the product by radical combination (ΔG = - 46.85 kcal mol^{-1}) is also conceivable.

It is important to note that when we carried out the reaction from 4-methoxybenzenediazonium **1a** under standard conditions in the absence of styrene (Scheme 2, **B**), we mostly observed the

reduction product (anisole) and the N,N-dimethyl-*p*-anisamide. The formation of the latter could result from the coupling between the carbamoyl radical **3'** and the arylradical **4**. As this is sometimes obtained when the reactivity is low or under very diluted conditions, it is compatible with our hypothesis of a mechanism proceeding through radical intermediates. As far as the very low reactivity noted with NaO*t*Bu is concerned, it may be due to the absence of proton exchange of this base with the DMF.[30h] Comparatively, a rapid exchange of the formamide proton takes place in a solution of KO*t*Bu in DMF, which is much more soluble than the NaO*t*Bu in this solvent.

In summary, we have disclosed a new way to perform the Matsuda-Heck reaction, which does not require the presence of a transition metal catalyst. The costly palladium/ligand catalytic systems traditionally used are here replaced by the KOtBu/DMF couple which allows, from aryldiazonium salts and under mild temperature conditions (20 °C), the selective and direct synthesis of stilbenes, which constitute highly important intermediates and targets in the chemical, pharmaceutical, and materials industries. Mildness, low-cost, experimental simplicity and the fact that it is not necessary to remove impurities of transition metal from final molecules are features of our method, which make it particularly well suited for syntheses of pharmaceuticals where financial, environmental and toxicity issues are of greater concern. Based on our experimental and theoretical studies we propose a radical mechanism which proceeds through the initial formation of a carbamoyl anion, able to initiate the formation of an aryl radical in the presence of the diazonium salt. The propagation phase would then follow an $S_{RN}1$ pathway leading to the formation of stilbenes through the intermediate formation of a new radical anion. Another way could involve a radical abstraction/recombination sequence. Efforts to expand the utility of this system to other cross-coupling and related reactions, along with mechanistic studies, are in progress and will be reported in due course.

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Keywords: Matsuda-Heck • Arylation • Csp2-Csp2 bond formation • Stilbene • Reaction mechanisms

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