

## Palladium-catalysed intramolecular carbenoid insertion of $\alpha$ -diazo- $\alpha$ -(methoxycarbonyl)acetanilides for oxindole synthesis

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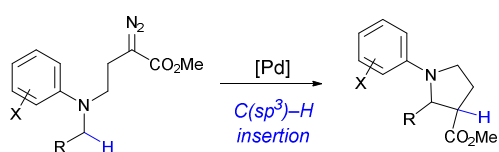
Daniel Solé,<sup>\*a</sup> Ferran Pérez-Janer,<sup>a</sup> and Israel Fernández<sup>\*b</sup>

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**A novel, selective palladium-catalysed carbenoid C(aryl)-H insertion of  $\alpha$ -diazo- $\alpha$ -(methoxycarbonyl)acetanilides leading to oxindoles is described.**

The transition metal-catalysed intramolecular C–H insertion of diazo compounds constitutes a powerful methodology for the construction of carbocyclic and heterocyclic frameworks.<sup>1</sup> Although the use of dirhodium(II)<sup>2</sup> and copper<sup>3</sup> catalysts has traditionally monopolized this area of research, in recent years different transition metals, including gold,<sup>4</sup> nickel,<sup>5</sup> ruthenium,<sup>6</sup> cobalt,<sup>7</sup> iron and manganese,<sup>8</sup> have emerged as useful alternatives. Surprisingly, palladium, one of the most commonly employed metals in homogeneous catalysis, has been scarcely applied to these processes, its use being restricted to a couple of examples of  $\alpha$ -diazo- $\beta$ -ketoester insertion into  $Csp^2$ -H bonds.<sup>9,10</sup> In this context, we recently reported that palladium catalysts are also able to promote  $Csp^3$ -H insertion of carbenoids derived from  $\alpha$ -diazoesters to form pyrrolidines through intramolecular  $C(sp^3)$ - $C(sp^3)$  bond formation (Scheme 1).<sup>11</sup>

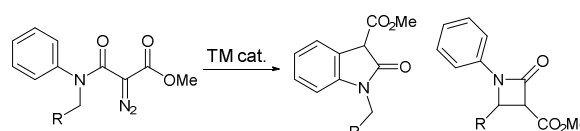


**Scheme 1.** Previously reported Pd-catalysed  $Csp^3$ -H insertion of carbenoids derived from  $\alpha$ -diazoesters (see ref. 11).

Among the reported transition metal-catalysed intramolecular C–H insertions of diazo compounds, the reaction of *N*-alkyl-*N*-aryl  $\alpha$ -diazoamides has been extensively

explored,<sup>12</sup> since the insertion products, namely  $\beta$ - and  $\gamma$ -lactams as well as 2-oxindoles, are common scaffolds found in numerous natural products. The selectivity of these reactions depends not only on the carbenoid and substrate substitution, but is also governed by the catalyst.<sup>13</sup> Thus, for instance, the use of Rh(II) carboxylate and, in particular, carboxamide catalysts has resulted in the development of highly chemo-, regio- and stereoselective transformations with a variety of reaction modes.<sup>14</sup> On the other hand, more recently, the commercially available  $[Ru(p\text{-cymene})Cl_2]_2$  has been used as a catalyst to develop diverse methodologies for oxindole synthesis based on the  $\alpha$ -diazoamide carbenoid insertion.<sup>15</sup>

Encouraged by the results of our previous work, we decided to explore the feasibility of palladium as a catalyst to promote the carbenoid C–H insertion from  $\alpha$ -diazo- $\alpha$ -(methoxycarbonyl)acetanilides (Scheme 2). In this investigation, we sought to identify differences in the reactivities and selectivities between the palladium catalyst and the transition-metal catalysts mentioned above.<sup>16</sup>



**Scheme 2.** Transition metal (TM) catalysed carbenoid C–H insertion of  $\alpha$ -diazo- $\alpha$ -(methoxycarbonyl)acetanilides.

$\alpha$ -Diazoamide **1a** was chosen as a model substrate for our initial studies (Table 1). In line with the results previously reported for related substrates,<sup>14b-d</sup> the Rh(II) acetate-catalysed decomposition of **1a** resulted in the intramolecular carbenoid insertion into the benzylic C–H bond to give mainly *trans*- $\beta$ -lactam **2a** (entry 1). In contrast, treatment of **1a** with a catalytic amount of  $Pd_2(dba)_3$  in toluene at reflux for 72 h afforded oxindole **3a**, arising from the arylic C–H bond insertion, in 42% yield (entry 2). While a similar result was obtained when the reaction was carried out in dioxane for 31 h (entry 3), the use of either the more polar  $CH_3CN$  or the high boiling chlorobenzene as the solvent led to the complete decomposition of the material (results not shown in the table).

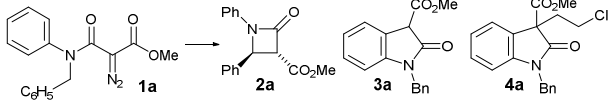
<sup>a</sup> Laboratori de Química Orgànica, Facultat de Farmàcia, Universitat de Barcelona. Av. Joan XXIII 27-31, 08028 Barcelona, Spain. E-mail: [dsale@ub.edu](mailto:dsale@ub.edu).

<sup>b</sup> Departamento de Química Orgànica and Centro de Innovación en Química Avanzada (ORFEO-CINQA), Facultat de Ciències Químiques, Universidad Complutense de Madrid, 28040 Madrid, Spain. E-mail: [israel@quim.ucm.es](mailto:israel@quim.ucm.es).

Electronic Supplementary Information (ESI) available: Experimental procedures, characterization data of new compounds, copies of NMR spectra and computational details and Cartesian coordinates of all species described in the manuscript. See DOI: 10.1039/x0xx00000x

Note that oxindole **3a** was difficult to isolate in pure form due to its well-known tautomeric equilibrium.<sup>14c-d</sup>

**Table 1.** Transition metal-catalysed cyclisation reactions of  $\alpha$ -diazamide **1a**<sup>a</sup>



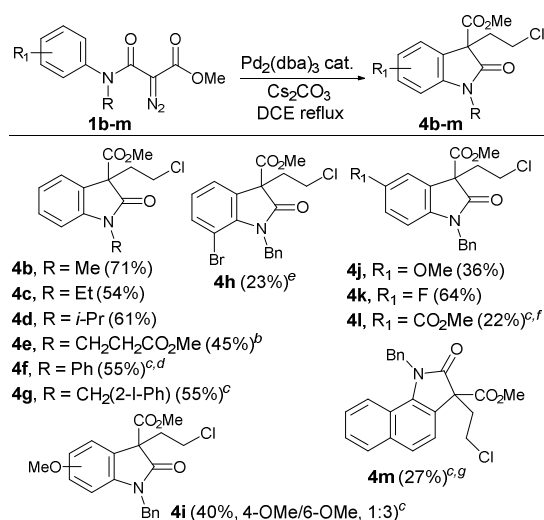
entry	catalyst (mol%)	additives (equiv.)	solvent	temp	time	products (%) <sup>b</sup>
1	[Rh(OAc) <sub>2</sub> ] <sub>2</sub> (2)	---	CH <sub>2</sub> Cl <sub>2</sub>	rt	33 h	<b>2a</b> (48%) <sup>c</sup>
2	Pd <sub>2</sub> (dba) <sub>3</sub> (7.5)	Cs <sub>2</sub> CO <sub>3</sub> (2)	toluene	reflux	72 h	<b>3a</b> (42%) <sup>d</sup>
3	Pd <sub>2</sub> (dba) <sub>3</sub> (10)	Cs <sub>2</sub> CO <sub>3</sub> (2)	dioxane	reflux	31 h	<b>3a</b> (44%) <sup>d</sup>
4	Pd <sub>2</sub> (dba) <sub>3</sub> (10)	Cs <sub>2</sub> CO <sub>3</sub> (2)	DCE	reflux	96 h	<b>4a</b> (66%)
5	Pd(OAc) <sub>2</sub> (20)	Cs <sub>2</sub> CO <sub>3</sub> (2)	DCE	reflux	72 h	<b>1a:4a</b> (1.2:1) <sup>e</sup>
6	Pd(PPh <sub>3</sub> ) <sub>4</sub> (20)	Cs <sub>2</sub> CO <sub>3</sub> (2)	DCE	reflux	72 h	<b>1a:4a</b> (1.1:1) <sup>e</sup>
7	Pd <sub>2</sub> (dba) <sub>3</sub> (10) ( <i>o</i> -tolyl) <sub>3</sub> P (40)	Cs <sub>2</sub> CO <sub>3</sub> (2)	DCE	reflux	72 h	<b>1a:4a</b> (1:1.6) <sup>e</sup>
8	Pd <sub>2</sub> (dba) <sub>3</sub> (10) dppe (20)	Cs <sub>2</sub> CO <sub>3</sub> (2)	DCE	reflux	72 h	<b>1a:4a</b> (1.3:1) <sup>e</sup>
9	Pd <sub>2</sub> (dba) <sub>3</sub> (10) <sup>t</sup> Bu <sub>3</sub> P-HBF <sub>4</sub> (40)	Cs <sub>2</sub> CO <sub>3</sub> (2)	DCE	reflux	72 h	CM <sup>f</sup>
10	---	Cs <sub>2</sub> CO <sub>3</sub> (2)	DCE	reflux	96 h	<b>1a:2a:4a</b> (2.5:0.2:1) <sup>e</sup>

<sup>a</sup> All reactions were conducted with **1a** (0.2 mmol, 0.2 M). <sup>b</sup> Isolated yield. <sup>c</sup> Minor amounts of the *cis*- $\beta$ -lactam (<10%) were also formed. <sup>d</sup> Small amounts of the bisoxindole dimer ( $\approx$  5%) were also formed, see the ESI. <sup>e</sup> <sup>1</sup>H NMR ratio, yields were not quantified. **Complex mixture with less than 10% of 4a.**

Pleasingly, we found that when using dichloroethane as the solvent, oxindole **4a** was directly obtained (66% yield) from a sequential carbenoid insertion/alkylation process (entry 4). The formation of **4a** not only facilitated the isolation of the cyclization product, but also avoided the generation of minor amounts of bisoxindole by-products,<sup>17</sup> which were also observed when using solvents other than DCE. The use of other palladium precatalysts such as Pd(OAc)<sub>2</sub> and Pd(PPh<sub>3</sub>)<sub>4</sub> resulted in slower reaction rates (entries 5 and 6). Similarly, all our attempts to increase the efficiency of the Pd-catalysed reaction by adding different phosphine ligands met with no success (entries 7-9). Finally, ca. 30% of conversion was observed in the absence of the palladium catalyst, giving a 0.2:1 mixture of *trans*- $\beta$ -lactam **2a** and oxindole **4a**, together with unreacted starting material (entry 10).<sup>18</sup> These results therefore indicate that Pd<sub>2</sub>(dba)<sub>3</sub> can catalyse the carbenoid C-H insertion of  $\alpha$ -diazo- $\alpha$ -(methoxycarbonyl)acetanilides, which chemoselectively proceeds into the aryl C-H bond to give the oxindole **3a**.<sup>19</sup> The selectivity of the insertion is the opposite of

that observed in our previous work with  $\alpha$ -diazoesters.<sup>11</sup> Moreover, when using dichloroethane as the solvent, the initially formed oxindole undergoes *in situ* alkylation<sup>20</sup> to afford **4a**. Interestingly, when the reaction was carried out with the base DBU [Pd<sub>2</sub>(dba)<sub>3</sub> (0.1), DBU (1.2) in DCE at reflux], *N*-benzyl-2-oxindole was obtained (69%) from the demethoxycarbonylation<sup>21</sup> of the initially formed oxindole **3a**.<sup>22</sup> This result confirms that Cs<sub>2</sub>CO<sub>3</sub> is not necessary for the Pd-catalysed insertion, but is needed for the alkylation process.

In order to assess the scope of this novel Pd-catalysed reaction, we then explored the sequential C-H insertion/alkylation process starting from a variety of  $\alpha$ -diazoacetanilides (Scheme 3). Firstly, we investigated the effect of changing the *N*-alkyl substituent on the course of the two-step sequential process. All the tested *N*-alkyl substrates were well tolerated under the conditions of the Pd-catalysed reaction. As can be seen in Scheme 3, the insertion occurs selectively into the aryl C-H bond, in the presence of primary, secondary as well as tertiary Csp<sup>3</sup>-H bonds. Oxindoles **4e** and **4f**, bearing a (methoxycarbonyl)ethyl and a phenyl group, respectively, were also obtained in acceptable yields. Under the optimized reaction conditions, amide **1g**, bearing a 2-iodobenzyl substituent at the nitrogen atom, selectively afforded oxindole **4g**. Strikingly, no product resulting from the competitive Pd-catalysed coupling of the aryl iodide with the diazo moiety<sup>23</sup> was observed in the reaction mixture.<sup>11</sup>



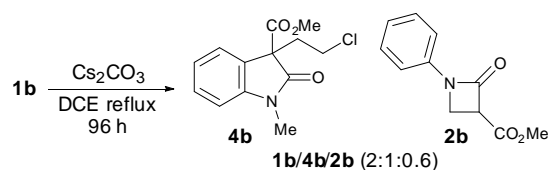
**Scheme 3.** Scope of the Pd-catalysed reaction. <sup>a</sup> See Table 1 for representative procedure. <sup>b</sup> 18% of unreacted starting material was recovered. <sup>c</sup> Catalyst loading: 15%. <sup>d</sup> 20% of unreacted starting material was recovered. <sup>e</sup> <sup>1</sup>H NMR analysis of the reaction mixture showed a 1:1 mixture of **1h** and **4h**. <sup>f</sup> The *O*-alkylation product **4l'** was also obtained (**4l/4l'**, 3:1), see the ESI. <sup>g</sup> The *O*-alkylation product **4m'** was also obtained (**4m/4m'**, 2:1), see the ESI.

It was also found that the stereoelectronic properties of the substituents on the aniline ring considerably affect the course of the cyclisation reaction. The presence of an *ortho*-bromo substituent on the aryl ring resulted in a very slow reaction, probably due to steric interactions. Thus, starting from **1h** and after 4 days under the usual reaction conditions, a 1:1 mixture of the starting amide and oxindole **4h** (23%) was

obtained. Amide **1i**, which bears a good electron-donating *meta*-methoxy group, underwent complete reaction to give oxindole **4i** (40%), which was isolated as a 1:3 mixture of regioisomers. On the other hand, amides **1j** and **1l**, which bear the electron-donating methoxy and electron-withdrawing (methoxycarbonyl) groups, respectively, at the *para* position afforded oxindoles **4j** and **4l** also in modest yields, despite complete consumption of the starting material. In contrast, oxindole **4k**, which has a fluoro substituent, was obtained in 64% yield. Finally, the *N*-naphthyl amide **1m** underwent selective C–H insertion to give **4m**, which was isolated together with the corresponding O-alkylation product.

To further confirm the catalytic role of palladium in the insertion reaction, the thermal decomposition of  $\alpha$ -diazoamides **1b** ( $R_1 = \text{H}$ ,  $R = \text{Me}$ ) and **1f** ( $R_1 = \text{H}$ ,  $R = \text{Ph}$ ) was also evaluated. In the absence of  $\text{Pd}_2(\text{dba})_3$  and under otherwise the same reaction conditions, **1b** afforded a 2:1:0.6 mixture of **1b**, **4b** and  $\beta$ -lactam **2b** (Scheme 4).<sup>24</sup> When the thermal reaction was run starting from **1f**, a 4:1 mixture of the starting material and oxindole **4f** was obtained. The recovery

of a considerable amount of starting material and, especially, the formation of  $\beta$ -lactams **2a** and **2b** in the thermal reactions clearly support the essential role of palladium as a catalyst for the oxindole formation.



Scheme 4. Thermal decomposition of amide **1b**.

To shed light on the reaction mechanism and selectivity of the Pd-catalysed C–H insertion reaction described above, density functional theory (DFT) calculations were carried out.<sup>25</sup> To this end, the reaction profile involving the simplest substrate **1b** and the model palladium(0) catalyst  $\text{Pd}(\text{PMe}_3)_2$  (thus resembling the reaction conditions gathered in Table 1, entry 6) was explored (Figure 1).

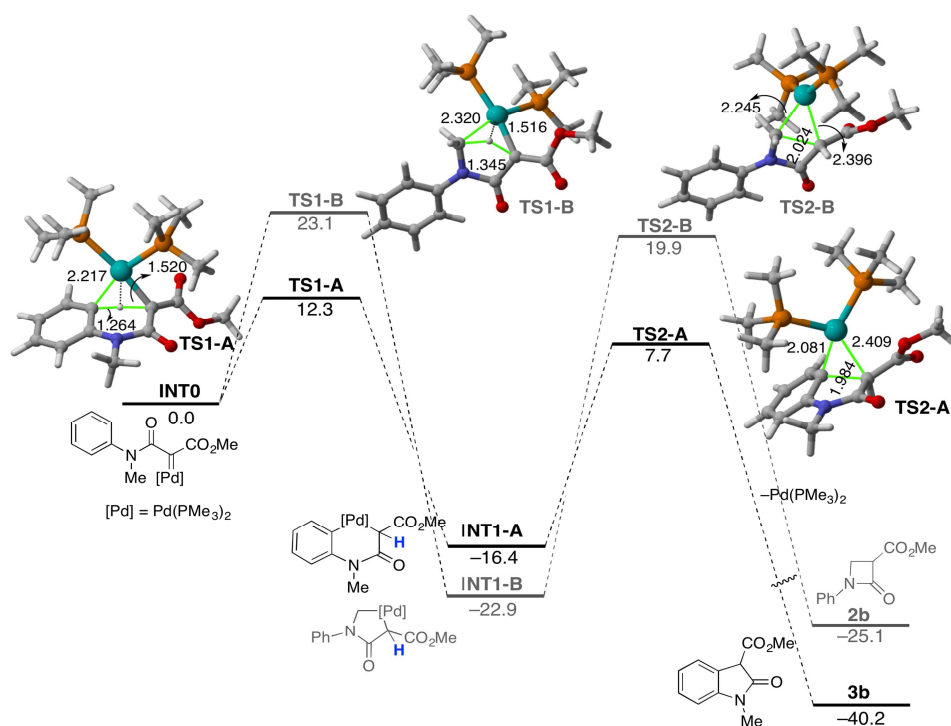


Figure 1. Computed reaction profiles for the Pd-catalysed formation of oxindoles over  $\beta$ -lactams. Relative free energies ( $\Delta G_{298}$ , at 298 K) and bond distances are given in kcal/mol and angstroms, respectively. All data were computed at the PCM(dichloroethane)-M06L/def2-TZVPP//PCM(dichloroethane)-B3LYP-D3/def2-SVP level.

As previously reported for the process involving the strongly related  $\alpha$ -diazoesters,<sup>11</sup> the reaction begins with intermediate **INT0**, the initial Pd(0)-carbene complex formed upon reaction of  $\text{Pd}(\text{PMe}_3)_2$  with **1b**. This species evolves to the Pd(II)-complex **INT1-A** through **TS1-A** with a low activation barrier of 12.3 kcal/mol in a highly exergonic transformation ( $\Delta G_{\text{R}} = -16.4$  kcal/mol). As clearly depicted in Figure 1, this step can be viewed as a Pd-mediated 1,5-H migration from the C(aryl)-H moiety to the carbenoid carbon atom, thus resulting in the formal oxidation of the transition metal. This transformation strongly resembles the one we recently

described for the Pd(0)-catalysed  $\text{Csp}^3$ -H insertion reactions of carbenoids derived from  $\alpha$ -diazoesters,<sup>11</sup> therefore suggesting a general reaction mechanism that does not depend upon the nature of the initial substrate. The process ends up with the conversion of the readily formed Pd(II)-complex **INT1-A** into oxindole **3b** (which in the presence of DCE and  $\text{Cs}_2\text{CO}_3$  evolves into the observed alkylated oxindole **4b**). This highly exergonic **INT1-A**  $\rightarrow$  **3b** transformation ( $\Delta G_{\text{R}} = -23.8$  kcal/mol) can be viewed as a reductive elimination reaction (via **TS2-A**,  $\Delta G^{\ddagger} = 24.1$  kcal/mol) which releases the active catalyst  $\text{Pd}(\text{PMe}_3)_2$ .

To understand the selectivity of the insertion, the formation of the possible  $\beta$ -lactam **2b** was also computed. As shown in Figure 1, the corresponding pathway leading to  $\beta$ -lactam **2b** is rather similar to that computed for oxindole **3b**, i.e. Pd-mediated 1,4-H migration via **TS1-B** followed by reductive elimination through **TS2-B**. From the data in Figure 1, it becomes evident that both reaction steps are associated with much higher activation barriers than those computed for the pathway involving **TS1-A** and **TS1-B**. In particular, the rather high barrier computed for the reductive elimination via **TS2-B** ( $\Delta G^\ddagger = 42.8$  kcal/mol) makes this step unfeasible. Therefore, it can be concluded that the complete selectivity of the process, which exclusively produces oxindoles over  $\beta$ -lactams, takes place mainly under kinetic control.

In summary, we have shown that palladium catalysis constitutes a useful alternative to promote the carbenoid C–H insertion of  $\alpha$ -diazo- $\alpha$ -(methoxycarbonyl)acetanilides, which selectively occurs into the aryl C(sp<sup>2</sup>)–H bond rather than the C(sp<sup>3</sup>)–H bonds. Moreover, when using DCE as the solvent, the insertion is followed by alkylation to give 3-(chloroethyl)oxindoles. Although the carbenoid insertion into the aryl C–H bond starting from  $\alpha$ -diazo- $\alpha$ -(alkoxycarbonyl)acetanilides can also be promoted by rhodium(II) perfluorocarboxamides,<sup>14c-d</sup> these catalysts are not commercially produced. Thus, considering the ready availability of Pd<sub>2</sub>(dba)<sub>3</sub> in particular, the present process would complement the existing methodologies based on the use of Rh as well as Ru catalysts.

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- Treatment of **1a** with Pd<sub>2</sub>(dba)<sub>3</sub> (0.1), Cs<sub>2</sub>CO<sub>3</sub> (2) and phenylvinylsulfone (1.1) in toluene at reflux afforded **3a** (60%). No traces of the corresponding Michael addition product were observed in the reaction crude.
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- Treatment of **1a** with Pd(PPh<sub>3</sub>)<sub>4</sub> (0.2) without any base in DCE at reflux afforded a complex mixture, in which **3a** and *N*-benzyl-2-oxindole were identified as the main products.
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- The identity of  $\beta$ -lactam **2b** was fully confirmed by comparison with an authentic sample prepared by treatment of **1b** with Rh<sub>2</sub>(OAc)<sub>4</sub>, see the ESI. All calculations were carried out at the PCM(dichloroethane)-M06L/def2-TZVPP // PCM(dichloroethane)-B3LYP-D3/def2-SVP level. See computational details in the ESI.

## Graphical Abstracts

A novel, selective palladium-catalysed carbenoid C(aryl)-H insertion of  $\alpha$ -diazo- $\alpha$ -(methoxycarbonyl)acetanilides leading to oxindoles is described.

