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COMMUNICATION

Ruthenium diacetate-catalysed oxidative alkenylation of C–H bonds in air: synthesis of alkenyl *N*-arylpyrazoles†

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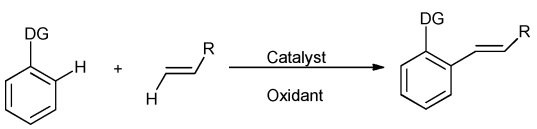
$Ru(OAc)_2$(*p*-cymene) catalyses the directed dehydrogenative alkenylation of *N*-aryl pyrazoles by styrene and alkyl acrylates in the presence of a catalytic or stoichiometric amount of $Cu(OAc)_2 \cdot H_2O$ in air; the acetic acid solvent plays a key role. With arene electron-donating groups, ruthenium-catalysed *ortho*-dialkenylation with alkyl acrylates can be obtained. A new method to generate the oxidative homocoupling of *N*-phenylpyrazole is provided with the $Ru(OAc)_2$(*p*-cymene) catalyst.

The transition metal-catalysed Heck reaction has proved to be one of the most useful methods for the synthesis of unsaturated molecules and conjugated materials *via* cross-coupling and C–C bond formation.[1] A potentially more efficient and greener process to reach the same family of unsaturated compounds consists of the catalytic oxidative alkenylation of aromatic C–H bonds, as pioneered by Fujiwara and Moritani.[2] It offers an atom-economical strategy to directly functionalise arenes with olefins, thus avoiding the prehalogenation of the substrate, as in the Heck reaction (eqn (1)).



(1)

Palladium catalysts have already been used to promote this useful transformation, and the regioselectivity is mainly controlled by functional directing groups linked to the arenes or heterocycles.[3] In parallel, rhodium catalysts[4–7] have also allowed the oxidative coupling of arene and heteroarene C–H bonds with functional alkenes for a variety of directing groups, such as amides,[5] imines[6] or carboxylates.[7] The development of this useful synthetic method is expected to depend on the use of stable, efficient and inexpensive metal catalysts, allowing the use of complementary directing functional groups in solvents compatible with industry developments. Comparatively less expensive ruthenium(II) catalysts for the oxidative alkenylation of arenes have just started to be explored.[8–13] Whereas the ruthenium(II)-catalysed oxidative Heck reaction with boronic acids has been described by Brown *et al.*,[8] Milstein *et al.* have pioneered the ruthenium-catalysed direct alkenylation of benzene by an alkyl acrylate.[9] Miura *et al.* have recently described the alkenylation of thiophene-2-carboxylic acids with acrylates in the presence of a $[RuCl_2$(*p*-cymene)$]_2$ catalyst,[10] showing that the carboxylic group directs the regioselective alkenylation at the neighbouring C–H bond without decarboxylation, as occurred with palladium catalysts. Related work on the synthesis of alkenyl arene derivatives has involved the formal insertion of alkynes into C–H bonds promoted by Ru(III) or Ru(II) catalysts, such as the alkenylation of phenylpyridine with $RuCl_3 \cdot H_2O$ in the presence of benzoic peroxide.[11] The annulation of alkynes with arylamides in the presence of a $[RuCl_2$(*p*-cymene)$]_2$ catalyst to generate a variety of isoquinolones *via* both aryl C–H and amide N–H functionalisation has recently been reported by Ackermann *et al.*,[12a] as the catalytic addition of acrylamides to alkynes for the formation of 2-pyridones.[12b] Moreover, Ackermann *et al.* have recently reported the dehydrogenative alkenylation of benzoic acids with acrylates in the presence of $[RuCl_2$(*p*-cymene)$]_2$ with 2 equiv. of $Cu(OAc)_2 \cdot H_2O$ in de-aerated water, leading to annulated lactones.[13]

In the course of our study on the regioselective functionalisation of aromatic C–H bonds with carboxylato-ruthenium(II) catalysts,[14,15] we have now found that the selective catalytic *ortho*-alkenylation of *N*-arylpyrazoles, which constitute an important class of heterocycles, can be easily performed. We now report that $Ru(OAc)_2$(*p*-cymene) catalyses the dehydrogenative alkenylation of *N*-arylpyrazoles by styrene and alkyl acrylates in acetic acid and air in the presence of a catalytic or stoichiometric amount of $Cu(OAc)_2 \cdot H_2O$. We also report a complementary method to perform the oxidative homocoupling of *N*-phenylpyrazole promoted by a $Ru(OAc)_2$(*p*-cymene) catalyst.

Results and discussion

The alkenylation with styrene of *N*-phenylpyrazole (**1a**) was first attempted with $Ru(OAc)_2$(*p*-cymene)[14b,f] in the presence of an oxidant. As the C–H bond activation of functional

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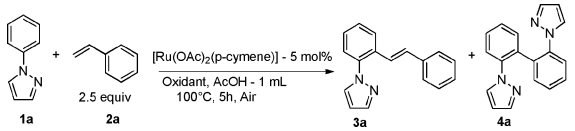
Table 1 Influence of the oxidant on the alkenylation of **1a** with styrene[a]



(2)

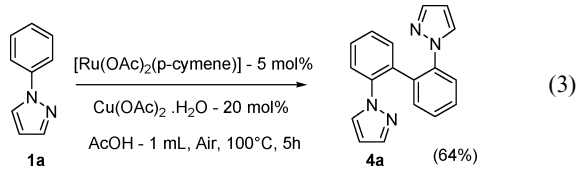
Entry	Oxidant/mmol	Conversion (%)[b] (**3a**/**4a**)[c]
1	Benzoquinone (1.1)	72 (83/17)
2	$Cu(OTf)_2$ (0.1 = 20 mol%)	70 (13/87)
3	$CuBr_2$ (0.1)	84 (73/27)
4	$CuCl_2$. $2H_2O$ (0.1)	88 (5/95)
5	$Cu(OAc)_2$ (0.1)	98 (56/44)
6	$Cu(OAc)_2{\cdot}H_2O$ (0.1 = 20 mol%)	98 (93/7)
7[d]	$Cu(OAc)_2{\cdot}H_2O$ (0.1)	51 (**3a**, **4a** + products)
8[e]	—	72 (88/12)
9[f]	$Cu(OAc)_2{\cdot}H_2O$ (1.1)	—
10[g]	$Cu(OAc)_2{\cdot}H_2O$ (0.1)	75 (30/70)

[a] Reaction conditions: 0.5 mmol of phenylpyrazole, 5 mol% of $Ru(OAc)_2$(*p*-cymene), oxidant, 10 μL of tetradecane as an internal standard for GC, 1.25 mmol of styrene in 1 mL of AcOH. [b] Conversion determined by gas chromatography. [c] Ratio **3a**/**4a** determined by gas chromatography. [d] Reaction performed under argon. [e] Without $Cu(OAc)_2{\cdot}H_2O$. [f] Without $Ru(OAc)_2$(*p*-cymene). [g] At 80 °C.

arenes promoted by $Ru(OAc)_2$(*p*-cymene) has recently been shown to involve an autocatalytic process, in which the formed acetic acid plays the role of a cocatalyst,[15] the use of an acetic acid-containing solvent was studied (see ESI, Table S1†) with various oxidants in air at 100 °C. The reaction led to the formation of the desired *ortho*-monoalkenylated product, **3a**, and the *N*-phenylpyrazole dehydrogenative homocoupling derivative **4a**, of which the ratio strongly depended on the oxidant's nature and conditions (eqn (2) and Table 1).

Whereas polar organic solvents NMP and DMF or DEC and toluene did not allow the reaction to take place, the addition of 0.1 mL of AcOH to various solvents increased the conversion, and finally acetic acid appeared to be by far the best solvent (ESI, Table S1†). The study showed that $Cu(OAc)_2{\cdot}H_2O$, especially when used in a catalytic amount of 20 mol% (Table 1, entry 6), was preferable to the use of benzoquinone, $Cu(OTf)_2$ or $CuBr_2$ (Table 1, entries 1–3). In contrast, $CuCl_2{\cdot}2H_2O$ strongly favoured oxidative homocoupling product **4a** formation (Table 1, entry 4). More importantly, a hydrated copper(II) salt was crucial to reach a high selectivity of **3a** (Table 1, entries 5 and 6). The determining role of the $Ru(OAc)_2$(*p*-cymene) catalyst was shown, as in its absence, no catalytic alkenylation or homocoupling reaction took place, whereas without $Cu(OAc)_2{\cdot}H_2O$, it led to only a 72% conversion (Table 1, entries 8 and 9). The absence of air and a decrease of temperature to 80 °C disfavoured the formation of **3a** (Table 1, entries 7 and 10).

The partial and sometimes predominant formation of homocoupling product **4a** (Table 1, entries 2 and 4) led us to improve its formation from **1a** with $Ru(OAc)_2$(*p*-cymene). Actually, in acetic acid as the solvent in the presence of 20 mol% of $Cu(OAc)_2{\cdot}H_2O$ at 100 °C in air without styrene, the complete transformation of **1a** was observed after 5 h, and **4a** was quantitatively formed and isolated in 64% yield (eqn (3)).



(3)

Some examples of the ruthenium-catalysed dehydrogenative homocoupling of arenes functionalized by a heterocycle have already been reported[15–19] using a sacrificial electrophile such as methallyl acetate[16] or aryl chloride,[18] or an oxidant such as $FeCl_3$.[17] The above results show that the $Ru(OAc)_2$(*p*-cymene) catalyst in AcOH with 20 mol% of $Cu(OAc)_2{\cdot}H_2O$ as the oxidant provides an excellent way to conduct the homocoupling of a functional arene.[19] It is noteworthy that the alkenylation of **1a** with styrene is faster than the homocoupling of **1a**, as under almost the same conditions, the presence of 2.5 equiv. of styrene inhibited the formation of **4a** to the benefit of **3a** formation (Table 1, entry 6).

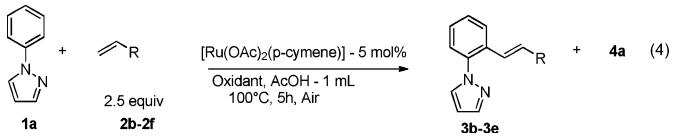
With the optimal conditions for the preparation of **3a** in hand (Table 1, entry 6), the alkenylation of **1a** was attempted with a variety of functional alkenes at 100 °C, but varying the reaction time and the ratio of $Cu(OAc)_2{\cdot}H_2O$ (20 mol% or 1 equiv.) (Table 2). For the less-reactive electrophilic acrylates **2b–2e**, the complete conversion could not be reached after 30 h with 20 mol% of $Cu(OAc)_2{\cdot}H_2O$, leading to the high production of **4a**. In this case, 1 equiv. of $Cu(OAc)_2{\cdot}H_2O$ was required to obtain full conversion with a high selectivity (>98%) for **3b–3d**, which were isolated in 65–77% yields (Table 2, entries 1–4). In contrast, methyl methacrylate (**2f**) was inactive and the reaction led to the formation of **4a** as the only product, most likely due to the double substitution on one carbon atom (Table 2, entry 5).

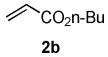
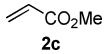
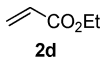
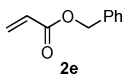
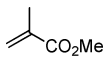
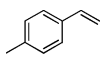
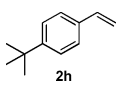
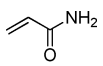
Alkyl-substituted styrenes **2g** and **2h** were less reactive than styrene itself and lead to full conversion but with moderate **3**/**4** selectivity (Table 2, entries 6 and 7). It is noteworthy that acrylamide (**2i**) led to an important ratio of the alkenylation (Table 2, entry 8), whereas *N*,*N*-dimethyl-substituted acrylamide **2j** inhibited the alkenylation to the benefit of derivative **4a** formation (Table 2, entry 9). Thus, each time the alkene is not reactive the homocoupling reaction takes place (Table 2, entries 5 and 9).

The alkenylation of substituted *N*-phenylpyrazoles **1b–1f** with alkyl acrylates was investigated (eqn (5)) to evaluate the aryl substituent influence on both the rate and on mono and dialkenylation. The results with $Cu(OAc)_2{\cdot}H_2O$ (0.1 and 0.5 mmol) are displayed in Table 3.

The reaction of sterically-hindered 6-methoxyphenylpyrazole (**1b**) with 2.5 equiv. of alkyl acrylates lead to *E*-monoalkenylated derivatives **5a–c**, isolated in 43–62% yield. These reactions were slower than those with parent compound **1a**, showing that the electron-donating *ortho*-methoxy group slows down the alkenylation; however, under these conditions, the corresponding homocoupling product was never observed. 4-Methoxyphenylpyrazole (**1c**) under similar conditions but with 1 equiv. of $Cu(OAc)_2{\cdot}H_2O$ afforded the corresponding *ortho*-mono alkenylated pyrazoles **6a** and **7a**, but with a significant amount of dialkenylated pyrazoles **6b** and **7b** (Table 3). Products **7a** and **7b** lead to a blue fluorescence in solution when irradiated at 365 nm, showing the potential of this C–H bond alkenylation for the production of molecular materials for optical applications.

Table 2 Alkenylation of phenylpyrazole **1a** with various alkenes[a]



No.	2	*T*/h	$Cu(OAc)_2 \cdot H_2O$ 0.1 mmol		$Cu(OAc)_2 \cdot H_2O$ 0.5 mmol	
			Conv. (%)	(**3**/**4**) (Y%)[b]	Conv. (%)	(**3**/**4**) (Y%)[b]
1	 **2b**	30	78	85/15 (48)	100	98/2 **3b** (72)
2	 **2c**	24	78	63/37 (44)	100	99/1 **3c** (77)
3	 **2d**	30	70	41/59 (22)	100	99/1 **3d** (65)[c]
4	 **2e**	30	86	76/24 (31)	100	99/1 **3e** (66)
5	 **2f**	36	100	0/100		
6	 **2g**	36	100	58/42	100	56/44 **3g** (25)
7	 **2h**	36	100	37/63	95	39/61
8	 **2i**	36	72	88/12	100	**3i** (71)
9	 **2j**	36	80	0/100	82	0/100

[a] Reaction conditions as in Table 1, except for the reaction time and oxidant amount in mmol. [b] Ratio determined by GC and (isolated yield (%)). [c] Additional 15% of divinylated product was also obtained.

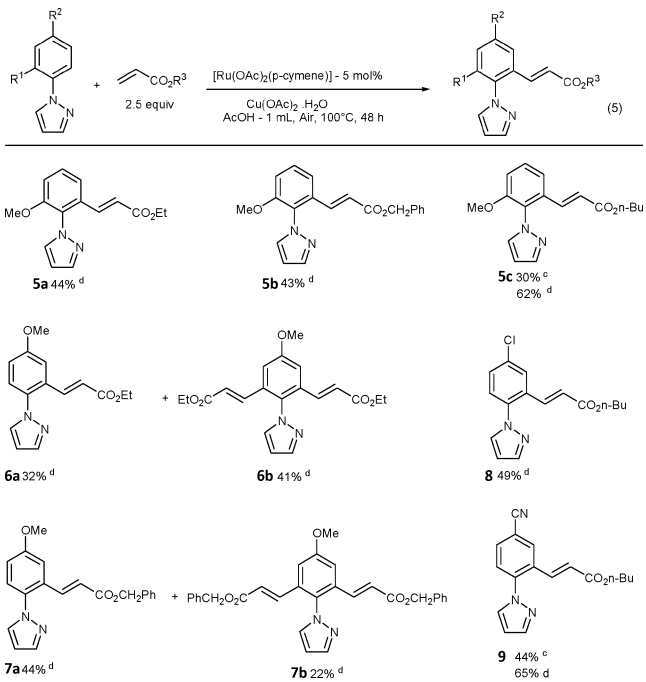
By way of contrast, the reaction of pyrazoles containing an electron-withdrawing group, such as 4-chloro- and 4-cyano-phenylpyrazole **1d** and **1e**, lead to the corresponding monoalkenylated products **8** and **9**, but in moderate yield.

The mechanism of formation of alkenyl functional arenes directed by the pyrazole function with a ruthenium(II) catalyst in an acetic acid medium is still not clear. However, it may involve these plausible successive steps: (i) *ortho*-C–H bond deprotonation by the assistance of the acetate/acetic acid in an autocatalytic process to generate the metallacycle,[14–15] (ii) insertion of the alkene into the C–Ru(II) bond[9] of the resulting metallacycle, (iii) β-elimination with formation of a Ru(H)(OAc)Ln species and (iv) regeneration of an $Ru(OAc)_2Ln$ catalyst by the action of the Cu^{2+} salt, oxygen and the acetic acid.

Conclusion

The above results show the first examples of the oxidative alkenylation of *N*-phenylpyrazoles performed by the cooperative action of a ruthenium(II) catalyst and acetate ligands, and in the presence of $Cu(OAc)_2 \cdot H_2O$ in air. The profitable action of the solvent acetic acid is especially shown, suggesting its action in C–H bond cleavage as an autocatalytic process. Alkenylation with electrophilic acrylates requires a stoichiometric amount of oxidant, whereas that with styrene is easier and is performed with a catalytic amount of $Cu(OAc)_2 \cdot H_2O$ in acetic acid. Conditions have been found for the dehydrogenative homocoupling of *N*-phenylpyrazole. The exploration of this direct $Ru(O_2CR)_2Ln$-catalysed alkenylation by alkenes of functional arenes and of the relevant mechanism are under investigation.

Table 3 Alkenylation of substituted aryl pyrazoles with various acrylates[a,b]



[a] Reaction conditions as in Table 1, except for time and the amount of oxidant. [b] Isolated yield. [c] $Cu(OAc)_2 \cdot H_2O$ 0.1 mmol (20 mol%). [d] $Cu(OAc)_2 \cdot H_2O$ 0.5 mmol (1 equiv.).

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19 Dehydrogenative homocoupling of functional arenes has already been performed with several ruthenium(II) catalysts: (*a*) at 120 °C for 20 h in xylene with a $[RuCl_2(COD)]_n/PPh_3$ catalyst and K_2CO_3, especially for the homocoupling of aryl-oxazolines by S. Oi *et al.*[16]; (*b*) at 110 °C for 16 h in chlorobenzene with $[RuCl_2(p\text{-cymene})]_2$ (2.5 mol%) and $FeCl_3$ (80 mol%) in the absence of a base for the homocoupling of 2-arylpyridines by C.-J. Li *et al.*[17]; (*c*) at 120 °C for 20 h in toluene with a $[RuCl_2(p\text{-cymene})]_2$ catalyst (2.5 mol%) and $MesCO_2H$ (30 mol%), with K_2CO_3 and an arylchloride (2-chlorotrifluoromethylbenzene), especially for the homocoupling of a variety of 1,2,3-triazol-4-yl arenes by L. Ackermann *et al.*[18]; (*d*) Thus, the present method is performed under milder conditions at 100 °C for 5 h in acetic acid in air with a $Ru(OAc)_2(p$-cymene) catalyst in the presence of 20 mol% of $Cu(OAc)_2 \cdot H_2O$ for *N*-phenylpyrazole.

