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Investigation of the possible role of arylamine formation in the *ortho*-substituted nitroarenes reductive cyclization reactions to afford heterocycles

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Abstract

Reductive carbonylation of nitroarenes with an unsaturated group in the *ortho* position generally affords high yields of heterocyclic compounds, including indoles, chalcones, quinolines, benzimidazoles, benzotriazoles, and indazoles. There is, however, no direct information on the organic intermediates formed during the reaction. In this paper, we have examined the possible formation of anilines as intermediates in the synthesis of indoles, acylindoles, quinolines, and quinolones with several catalytic systems based on palladium, ruthenium and rhodium. It transpired that, independent of the metal complex used as a catalyst, the formation of aniline as an intermediate is essential in the intra-molecular condensation reactions of nitroarenes involving an aldehydic or a keto group (including Michael addition reactions), but plays at best a very limited role in the addition reactions involving a C=C double bond. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Reductive carbonylation; Catalysis; Palladium; Ruthenium; Rhodium

1. Introduction

Reductive carbonylation of nitroarenes with an unsaturated group in the *ortho* position generally affords high yields of heterocyclic compounds, including indoles, chalcones, quinolines, benzimidazoles, benzotriazoles, and indazoles [1,2]. The synthesis of many of these products has been proposed to proceed through the intermediate formation of an imido complex, which should be able to attack the unsaturated group to afford the heterocyclic product. However, no direct evidence has been obtained for the involvement of imido species in the catalytic cycle and as such there are other alternatives which can be considered. In particular, we have recently shown that the synthesis of Schiff bases from nitroarenes and aldehydes under CO pressure proceeds through the formation of an aniline as an intermediate (by reduction by CO and traces of moisture) that later condenses with the aldehyde to afford the Schiff base, regenerating the water necessary to carry out the reaction (Scheme 1) [3].

Thus it appears likely that at least those syntheses of heterocyclic compounds that imply the intramolecular condensation of a nitro and a keto group should also proceed through aniline formation. However, the problem may be more general. It is well known that palladium(II) complexes promote the synthesis of indoles from *o*-aminostyrenes and that the reaction can be made

$$\begin{array}{l}
\mathrm{ArNO_2 + 3\,CO + H_2O} \xrightarrow{\mathrm{M.cat}} \mathrm{ArNH_2 + 3\,CO_2} \\
\mathrm{ArNH_2 + RCHO} \longrightarrow \mathrm{ArN{=}CHR + H_2O} \\
\hline
\mathrm{ArNO_2 + RCHO + 3\,CO} \xrightarrow{\mathrm{M.cat}} \mathrm{ArN{=}CHR + 3\,CO_2}
\end{array}$$

Scheme 1.

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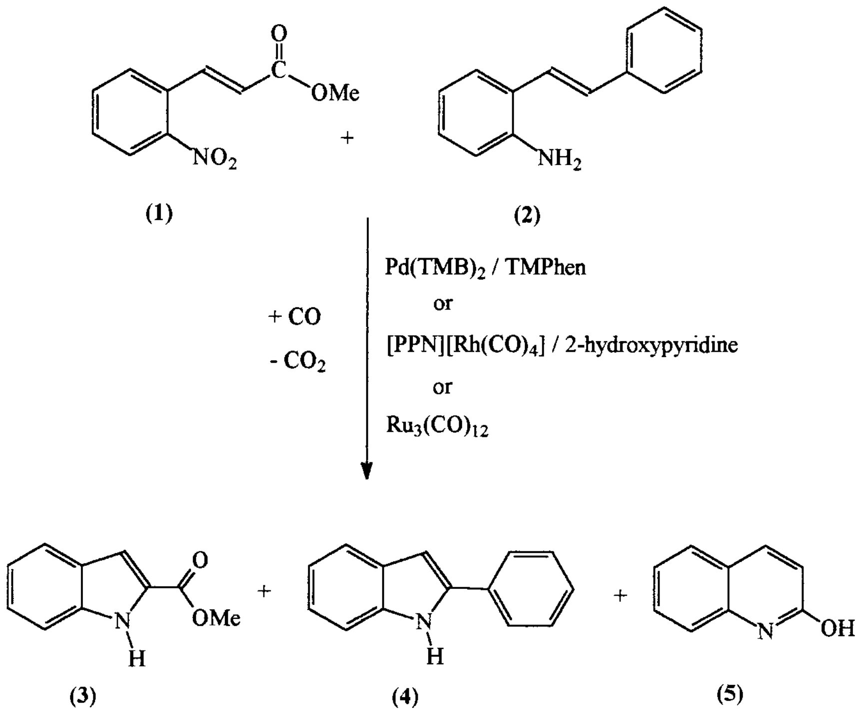


Scheme 2.

catalytic by the addition of an oxidant able to convert the palladium(0) complex formed at the end of the reaction back to palladium(II) [4]. Palladium complexes, especially those with phenanthroline ligands, are well known catalysts for the reductive carbonylation of nitroarenes. The available mechanistic information [5] indicates that the species reacting with the nitroarene is a palladium(0) complex, which is oxidized to a palladium(II) species during the reaction. Remarkably, in at least some of the catalytic systems, the nitroarene is initially reduced to aniline, independent of the identity of the final product of the catalytic reaction. Thus the possibility that the syntheses of indoles from *o*-nitrostyrenes (at least those catalyzed by palladium complexes) proceed through the intermediate reduction of the nitroarene to aniline, with simultaneous oxidation of palladium(0) to palladium(II), which is followed by a classical cyclization of the amine to afford the indole with the initial palladium(0) complex regenerated, should be considered.

To clarify the possible role of the intermediate formation of anilines in the synthesis of different heterocycles, we have performed three different syntheses, with a total of six different catalytic systems. We have worked with equimolar amounts of a nitroarene and an aniline which bear in the *ortho* position reactive groups of the same class, but have different substituents, so that the products derived from the possible reaction of the aniline could be distinguished from the ones derived from the nitroarene. If anilines were intermediates in the reaction, a mixture of two related heterocycles should be obtained, with a prevalence for the one derived from the aniline. On the other hand, if anilines were not intermediates, only the heterocycle derived from the nitroarene should be obtained. The results discussed here reveal a complex situation. To the best of our knowledge, this is the first time that the possible role of anilines in this class of reactions has been investigated.

2. Results and discussion

2.1. Synthesis of indoles

Three different, previously reported catalytic systems for the synthesis of indoles from *o*-nitrostyrenes were tested for the possible involvement of anilines in the reaction: one employing $Pd(TMB)_2$ in the presence of TMPhen (TMB = 2,4,6-trimethylbenzoate, TMPhen = 3,4,7,8-tetramethyl-1,10-phenanthroline) [6], one employing $[PPN][Rh(CO)_4]$ in the presence of 2-hydroxypyridine ($PPN^+ = (PPh_3)_2N^+$) [7], and one employing $Ru_3(CO)_{12}$ [8] as catalysts. The substrates used were methyl-2-nitrocinnamate (**1**) and 2-aminostilbene (**2**) (Scheme 2). The results of the GC analysis of the final reaction mixtures are reported in Table 1.

The results obtained clearly show that the indole products almost completely derive from the nitroarene both in the case of the palladium and the ruthenium catalytic systems; however, a significant amount of indole derived from the aniline is also obtained. In the

Table 1
Synthesis of indoles

Catalytic system	**1** conversion (%)[d]	**3** selectivity (%)[e]	**2** conversion (%)[f]	**4** selectivity (%)[g]	**4**/**3** mol ratio	**5** select (%)[e]
$Pd(TMB)_2$/TMPhen[a]	100	76.4	36.8	10.2	0.055	10.1
$[PPN][Rh(CO)_4]$/2-OH-pyridine[b]	99.0	11.5	76.9	4.7	0.343	27.3
$Ru_3(CO)_{12}$[c]	100	36.3	67.3	2.1	0.063	2.8

[a] Experimental conditions: $Pd(TMB)_2 = 0.011$ mmol, molar ratios Pd/TMPhen/**1**/**2** = 1:2:20:20, 180°C, 40 bar CO, in toluene (10 ml) for 3 h.

[b] Experimental conditions: $[PPN][Rh(CO)_4] = 0.0266$ mmol, molar ratios Rh/2-OH-pyridine/**1**/**2** = 1:6:20:20, 170°C, 60 bar CO, in *o*-dichlorobenzene (10 ml) for 5 h.

[c] Experimental conditions: $Ru_3(CO)_{12} = 6.57 \times 10^{-3}$ mmol, molar ratios $Ru_3(CO)_{12}$/**1**/**2** = 1:15:15, 220°C, 70 bar CO, in toluene (3 ml) for 1.5 h.

[d] Calculated with respect to initial **1**.

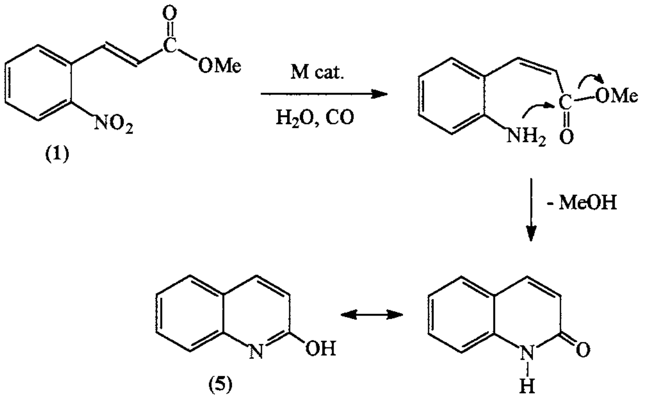
[e] Calculated with respect to converted **1**.

[f] Calculated with respect to initial **2**.

[g] Calculated with respect to converted **2**.

case of the rhodium catalyzed system, a majority of the indole is still derived from the nitroarene. However, the molar amount of indole **4**, derived from the aniline, is 34.3% of the nitroarene-derived indole (**3**). This relatively high amount of indole derived from the aniline is not due to a higher selectivity in the aniline reaction, but to the unusually low selectivity in the nitroarene reaction, which only gave a 11% selectivity in indole. Apparently, the presence of an amine in solution has a negative effect on the reaction. A certain amount of 2-hydroxyquinoline was also observed among the products. This compound had been previously obtained in similar reactions starting from **1**. It probably derives from an intramolecular cyclization of the by-product aniline derived from **1**, to afford the cyclic amide, which is in tautomeric equilibrium with **5** (Scheme 3). The necessary *trans–cis* isomerization of the double bond may be caused by both the presence of a metal and the high temperature.

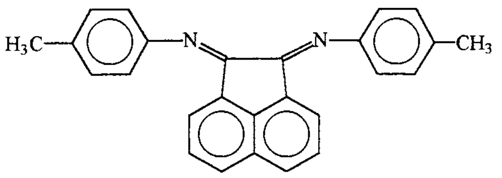
In the course of normal reactions the amount of aniline present is much lower than the one in the reactions performed in this study, as this compound is only formed as a by-product. Thus the contribution of the pathway passing through the aniline will be further depressed. Nevertheless, this is the first time that evidence for the existence of such a pathway is provided. The formation of the indole derived from the aniline even when the rhodium and ruthenium catalysts are employed imply that catalysts based on these metals should also be able to catalyze the formation of indoles from *o*-aminostyrenes in the presence of an oxidant. For this reaction only palladium-based catalysts have been studied in detail. However, it should be noted that the amount of **4** formed corresponds in all cases (including the palladium-promoted reaction) to a substoichiometric reaction with respect to the metal. This fact strengthens the idea that, at least under the experimental conditions typically employed for the cyclization reactions of nitroarenes [1,6–8], the intermediate formation of aniline plays a very limited role in the syntheses of indoles.



Scheme 3.

2.2. Synthesis of acylindoles and quinolines

A second case we examined was the reaction of 2-nitrochalcones to afford a mixture of 2-acylindoles and 2-substituted quinolines. The catalytic systems tested for these reactions were the $Pd(TMB)_2$/TMPhen one previously used also in the synthesis of simple indoles [9] and the one based on the combination $Ru_3(CO)_{12}$/Tol-BIAN [9], where Tol-BIAN is the ligand shown below[1]:



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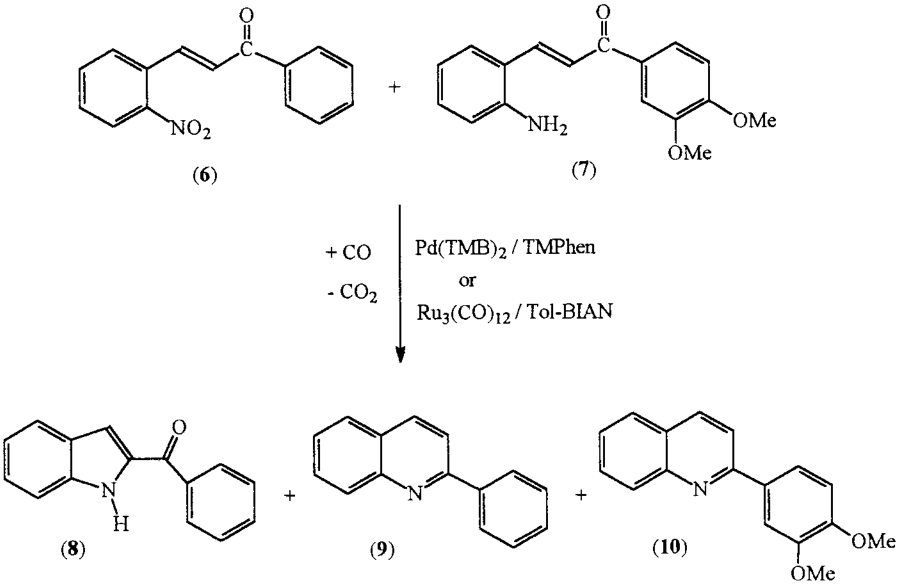
[1] Note that in previous papers we used the name DIAN-Me for this ligand. However, since other groups are using the general name Ar-BIAN for this class of ligands [10] and this last terminology is of more general application, we have decided to adhere to this convention in order to avoid the use of different names in the literature for the same compound.



Scheme 4.

In this case (Scheme 4) the products could not be analyzed by gas chromatography and the evidence for the formation of the different compounds in the reactions was provided by TLC with long (20 cm) alumina plates. Although the method did not allow for a quantitative estimation of the amounts of the various products, their identity could be easily established by comparison with authentic samples as several of the products have distinctive fluorescent behavior. The presence of the products observed by TLC was further confirmed by mass spectra of the solids obtained by evaporation of the solvent from the solutions after the reactions.

In the case of the ruthenium catalyst, the solution at the end of the reaction clearly showed the presence of the quinolines derived from both of the starting reagents, however only the acylindole **8** derived from the nitroarene could be detected. Trace amounts of both of the possible amines could also be observed on the TLC plates and in the mass spectra. From the data obtained it is clear that, in accord with what we expected based on our studies on the synthesis of Schiff bases from nitroarenes and aldehydes [3], the synthesis of quinolines proceeds via the aniline, while the water formed in the condensation reaction reduces more nitro compound to afford initially the second aniline, which later condenses to the nitroarene-derived quinoline (**9**). In the case of the palladium-catalyzed reaction, this ‘water recycling’ is essential for the reaction to be catalytic as only trace amounts of moisture, mainly from the CO gas, are present initially. In the case of the ruthenium-catalyzed reaction, a more than stoichiometric amount of water is added at the beginning in order to facilitate a faster reaction. The water, however, still acts in a catalytic manner.

It should be noted that in the previous literature, nitrenes have been most often proposed as the species responsible for quinoline formation from nitroarenes [11], although it has been proposed that anilines play a role in one case [12].

A different situation occurs in the case of the synthesis of acylindoles. Given the results reported in the previous section on the synthesis of simple indoles, it may appear surprising that the acylindole derived from **7** was not formed at all. Although it must be acknowledged that a very small amount (ca. 1–2%) may have escaped detection by TLC and mass spectra, the best explanation for the data obtained is that, in the present reaction, condensation of an intermediately formed aniline with the keto group already present in the molecule (to afford the quinoline) must be much easier than attack at the C=C double bond.

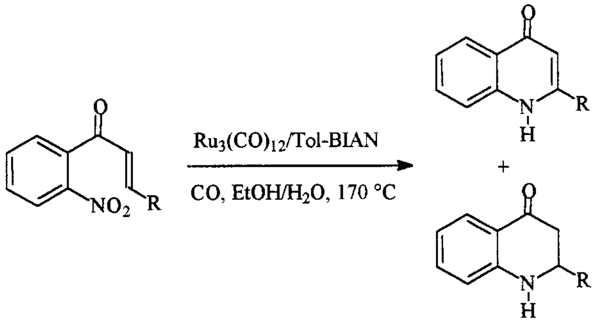
The Pd(TMB)$_2$/TMPhen catalytic system had been previously observed to yield higher selectivities in acylindole than the one based on ruthenium [9]. Accordingly, when the reaction in Scheme 4 was performed by using the palladium-based catalytic system, only the acylindole **8** and the quinoline **10** were formed. No acylindole derived from the amine or quinoline derived from the nitroarene could be detected by TLC or mass spectra, although a trace amount of the amine derived from **6** was present. The conversion of both **6** and **7** was almost quantitative. These results are even more clear cut than those from the previous reaction in indicating that the amine is the intermediate responsible for the quinoline formation, but is not involved in the synthesis of the acylindole.

2.3. Synthesis of 4-quinolones and 2,3-dihydro-4-quinolones

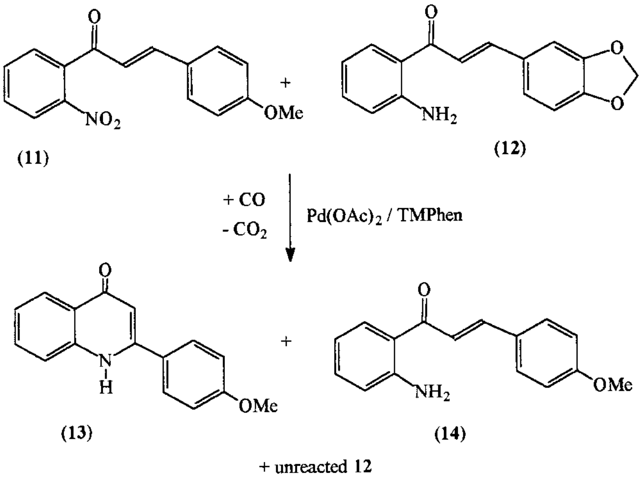
We have previously shown that 2′-nitrochalcones, isomeric products with respect to the ones considered in the previous paragraph, are reduced to a mixture of 4-quinolones and 2,3-dihydro-4-quinolones by CO in the presence of the same $Ru_3(CO)_{12}$/Ar-BIAN catalytic system mentioned above (Scheme 5) [13].

When the same reaction was performed by using the $Pd(OAc)_2$/TMPhen catalytic system, the saturated product was formed only in small amounts or not at all, although some other unidentified by-products were observed. In the course of that work, we also showed that 2′-aminochalcones gave intramolecular Michael addition to the conjugated double bond to afford the 2,3-dihydro-4-quinolone only and that this reaction was accelerated by the $Ru_3(CO)_{12}$/Ar-BIAN catalytic system [13]. We also showed that the saturated product could be converted to the unsaturated one by oxidation with 2,3-dichloro-5,6-dicyanobenzoquinone, but nitrobenzene, at least in the absence of a metal, was ineffective as an oxidant for this last reaction even at high temperatures. Since the presence of a metal complex may profoundly modify the ability of a nitroarene to act as an oxidant and may even allow for different reactions of the amine, as found for the minor pathway in the synthesis of indoles, we performed the cross reaction shown in Scheme 6.

Since it was already clear that the dihydroquinolone was derived from the amine, the palladium-based catalytic system was tested (which does not afford this product in significant amounts) to ascertain if even the quinolone may in part derive from the amine. In this way the competitive (and possibly faster) pathway leading to the dihydroquinolone is not present. The solution mixtures after the reactions were analyzed by ^1H-NMR, taking advantage of the almost complete insolubility of the unsaturated quinolones in $CDCl_3$, which allows for their separation and separate analysis in DMSO-d_6. The results clearly showed that the only quinolone formed was **13**, derived from the nitroarene, accompanied by some amine **14**, derived from the same reagent, and unreacted **12**. Minor amounts of unidentified by-products derived from the nitroarene were also observed in the $CDCl_3$-soluble fraction, but no product derived from **12** was observed. Thus the aniline is not an intermediate in the synthesis of the quinolone with this palladium catalyst, neither in a direct way, nor in a possible pathway including the intermediate formation of the dihydroquinolone followed by fast oxidation by the remaining nitroarene mediated by the metal itself.



Scheme 5.

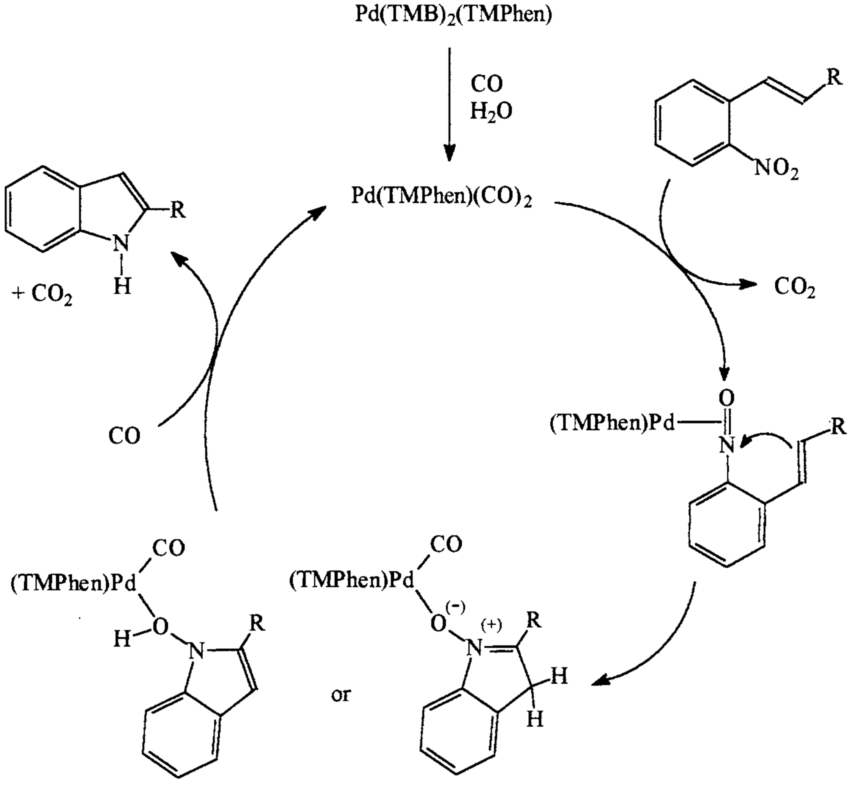


Scheme 6.

3. Conclusions

The work reported in this paper has clearly shown that, in accord with our results on the synthesis of Schiff bases from nitroarenes and aldehydes [3], the intermediate formation of aniline is essential in the intra-molecular condensation reactions of nitroarenes also involving an aldehydic or a keto group (including Michael addition reactions), but plays at best a very limited role in the addition reactions involving a C=C double bond. In relation to this last class of reactions, we can only speculate on the identity of the intermediate responsible for cyclization. An imido complex, as often proposed, is a possibility. However, when the carbonylation of some organic nitro derivatives was conducted in *cis*-cyclooctene as a solvent and with $Ru_3(CO)_{12}$ as a catalyst, nitrones were detected among the products [14]. These products appear to derive from a coupling of the intermediate nitrosoarene with the olefin, a reaction for which many precedents exists [15]. Deoxygenation of the nitrone by coordinated CO would then lead to the final product. We note only that the analogous azoxy derivative, PhN(O)=NPh, is readily deoxygenated by CO in the presence of a zerovalent ruthenium catalyst [16].

Other products commonly obtained by reaction of nitrosoarenes with olefins are hydroxylamines [17]. It is



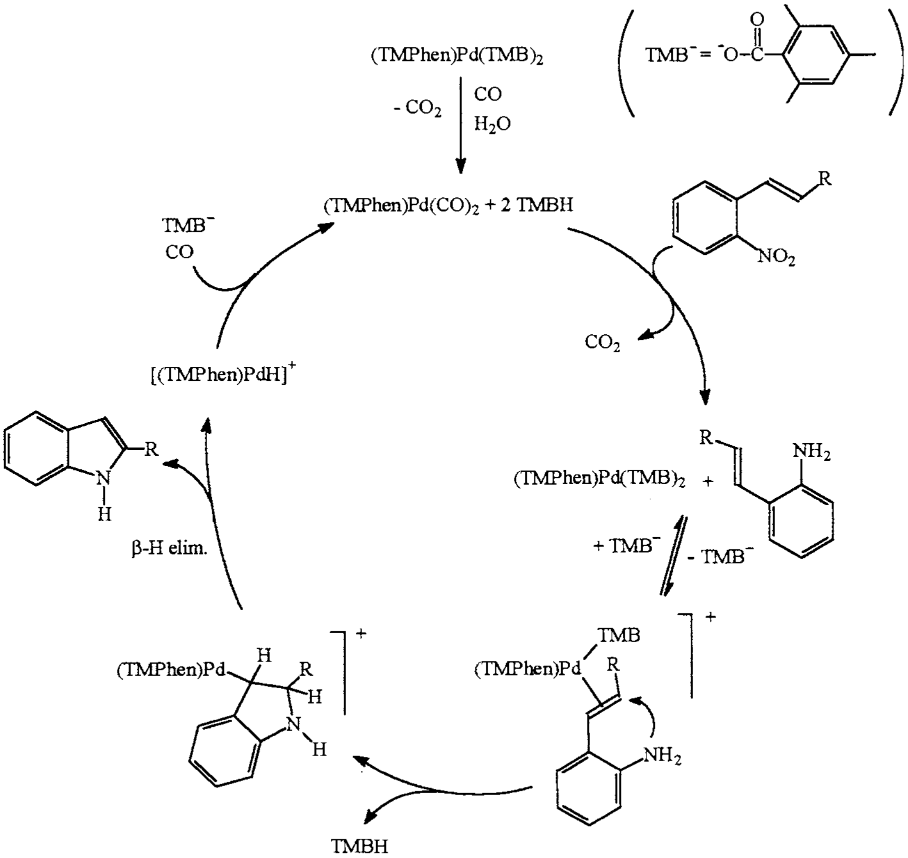
Scheme 7.

noteworthy that *N*-hydroxyindoles and *N*-hydroxyquinolones have been very recently observed as by-products in the cases of some cyclization reactions of *o*-nitrostyrenes and *o*-nitrochalcones catalyzed by Pd(TMB)$_2$/TMPhen [18] and this kind of product can even become the dominant one when the reaction is run in THF. Hydroxylamines are also known to be deoxygenated by metal carbonyls [19]. Finally, nitrosoarenes have been also shown to be responsible for at least part of the product in the inter-molecular addition of nitroarenes to olefins catalyzed by Ru$_3$(CO)$_{12}$ in the presence of Ar-BIAN [20]. Thus it appears that the reaction of the intermediate nitrosoarene with the olefin moiety is involved at least in part in the formation of the indoles and of the quinolones. A likely reaction scheme for the formation of the indoles catalyzed by Pd(TMB)$_2$/TMPhen which shows the formation of both of the possible nitrosoarene-derived intermediates (the nitrone and the hydroxyindole) is shown in Scheme 7. Similar mechanisms should operate in the cases involving other catalytic systems.

Adventitious moisture must be responsible for the initial reduction of the palladium catalyst. Note that all of the ‘organic’ species have been drawn as bound to the metal throughout the catalytic cycle, but it is also possible that the organic molecule leaves the metal coordination sphere at some stages of the reaction (this is quite likely for the hydroxylamine).

Although nitrosoarenes appear to directly react with the olefin moiety during the reaction, it must also be noticed that anilines are always by-products of the reactions investigated here and their formation requires a further reduction of the nitrogen-containing group, which may even involve the formation of an imido complex. Whether this imido complex also takes part into the cyclisation reaction to some extent cannot be deduced from our data.

A likely reaction scheme for the amine-mediated synthesis of indoles catalyzed by the same palladium system is reported in Scheme 8. Here again the reaction starts with a nitroarene deoxygenation by a zerovalent palladium complex [5]. In this case, we have evidenced that this reduction also produces two equivalents of trimethylbenzoic acid. The same acid may become involved in the reduction of the nitroarene by CO and the metal, affording the aniline and a palladium(II) complex. Exchange with external arylamine would occur at this stage of the process. From this point onward, the steps should be analogous to the ones proposed by Hegedus for his system [4], although the other ligands around the palladium atom are different in the two cases. In the Hegedus system, the oxidizing agent is benzoquinone. In the present system, it would be the nitroarene itself to play the dual role of oxidizing agent and source of the amine. For the other catalytic systems, proton sources other than trimethylbenzoic or



Scheme 8.

acetic acid must be present. The most likely candidate for this role in the rhodium-catalyzed system is 2-hydroxypyridine, whereas the protons are probably provided by water (even adventitious moisture) or by the other protic solvents in the case of ruthenium-catalyzed reactions.

4. Experimental

4.1. General procedures

Unless otherwise specified, all reactions and manipulations were performed under a N_2 atmosphere using standard Schlenk apparatus, cannula techniques, and magnetic stirring, but the products of the catalytic reactions had to be handled in the air for at least some time. Solvents were dried and distilled by standard procedures and stored under dinitrogen. [PPN][$Rh(CO)_4$] [21], $Ru_3(CO)_{12}$ [22], $Pd(TMB)_2$ [23], **1** [24], **2** [25], **6** [26], **7** [27], **11** [28], and **12** [29] were synthesized by methods reported in the literature. Products **3** [6], **4** [6], **8** [26b,30], **10** [31], **13** [32], and **14** [18] are known compounds and were identified by comparison with authentic samples or with the spectroscopic data reported in the literature. **5** and **9** were identified by comparison with commercial samples (Aldrich). TolBIAN was synthesized as previously reported [10,20b]. All other compounds were commercial products and were used as received. GC analyses were performed on a Perkin-Elmer 8420 capillary GC equipped with a PS 255 column. R_i values (R_i = response factor, relative to naphthalene as an internal standard) were determined by the use of solutions of known concentrations of the compounds. GC–MS analyses were performed on a Hewlett-Packard 5890 Series II GC, equipped with a 5971A mass selective detector. NMR spectra were recorded on a Bruker AC 200 FT spectrometer (200 MHz) at room temperature. Elemental analyses and mass spectra were recorded in the analytical laboratories of Milan University.

4.2. Catalytic reactions

In a typical reaction, the reagents were weighed in a glass liner. The liner was placed inside a Schlenk tube with a wide mouth under dinitrogen and was frozen at − 78°C with dry ice, evacuated and filled with dinitrogen, after which the solvent was added. After the solvent was also frozen, the liner was closed with a screw cap having a glass wool-filled open mouth which allows for gaseous reagents exchange and rapidly transferred to a 200 ml stainless steel autoclave with magnetic stirring. The autoclave was then evacuated and filled with dinitrogen three times. CO was then charged at room temperature at the required pressure and the autoclave was immersed in an oil bath preheated at the required temperature. In the case of the reactions catalyzed by [PPN][$Rh(CO)_4$], to avoid contact with air of this sensitive compound, it was weighed under dinitrogen and added to the glass liner only after the liner had already been frozen in the Schlenk tube under dinitrogen. At the end of the reaction the autoclave was cooled with an ice bath, vented and the products were analyzed as described in the following.

4.3. Synthesis of indoles

The reactions were performed as described above. Reagents amounts and experimental conditions are reported in Table 1. At the end of the reaction, naphtalene was added as an internal standard and the solutions were analyzed by gaschromatography. In all cases, but especially in the case of the reaction catalyzed by [PPN][$Rh(CO)_4$], a by-product was observed in the gaschromatograms, showing in the mass spectrum a parent peak at $M^+ = 253$. This mass corresponds to that of the methyl carbamate derived from **2**. Indeed, anilines are known to be intermediate in the $[Rh(CO)_4]^-$-catalyzed carbonylation of nitroarenes to carbamates in the presence of alcohols [33] and some methanol is liberated during the formation of **5**.

4.4. Synthesis of acylindoles and quinolines

The reactions were performed as described above using the following conditions: (a) **6** (13.4 mg, 0.053 mmol), **7** (15.0 mg, 0.053 mmol), $Ru_3(CO)_{12}$ (1.0 mg, 1.56×10^{-3} mmol), Tol-BIAN (1.7 mg, 4.7×10^{-3} mmol), in EtOH (10 ml) + H_2O (2.5 ml), $P_{CO} = 30$ bar, $T = 170$°C, for 3 h. (b) **6** (12.9 mg, 0.051 mmol), **7** (14.4 mg, 0.051 mmol), $Pd(TMB)_2$ (1.1 mg, 2.54×10^{-3} mmol), TMPhen (1.2 mg, 5.8×10^{-3} mmol), in toluene (20 ml), $P_{CO} = 20$ bar, $T = 100$°C, for 2 h. Products were analyzed by TLC (aluminum oxide 60 F_{254} (type E) Merck, 20 cm, eluant CH_2Cl_2/EtOH = 99.5:0.5) by comparison with authentic samples and by also taking advantage of the distinctive fluorescence of the products when irradiated at 366 nm (violet for quinolines and yellow–green for acylindoles). After the reaction and TLC analysis, the solutions were dried in vacuo and an EI mass spectrum of the resulting solids was recorded, confirming in all cases the presence of all and only the products observed by TLC (see Section 2). The conversion of the nitroarene **6** was complete for the reaction catalyzed by $Ru_3(CO)_{12}$, but not for the one catalyzed by $Pd(TMB)_2$. Conversion of the amine **7** was almost complete in both cases.

4.5. Synthesis of 4-quinolones

The reactions were performed as described above using the following conditions: **11** (34.0 mg, 0.12 mmol), **12** (32.0 mg, 0.12 mmol), $Pd(OAc)_2$ (3.0 mg, 1.34×10^{-2} mmol), TMPhen (5.4 mg, 2.28×10^{-2} mmol), in toluene (10 ml), $P_{CO} = 30$ bar, $T = 170$°C, for 3 h. At the end of the reaction, a precipitate was present, which was filtered on a glass frit and washed with CH_2Cl_2 (2 × 3 ml) The ^{1}H-NMR (DMSO-d_6) of the solid showed it to be a 7:3 mixture of **13** and of the amine derived from **11**, but no product derived from **12** was present. The solution after filtration and the CH_2Cl_2 washings were combined and dried in vacuo. The ^{1}H-NMR ($CDCl_3$) of this solid showed the presence of a very small amount of **11**, but three more peaks of comparable intensity were also present around 3.9 ppm (–OMe) indicating the presence of unidentified by-products. The saturated product 2,3-dihydro-2-(4-methoxyphenyl)-4-quinolone corresponding to **13** was not formed anyway, as shown by the absence of the signal for the hydrogenated double bond between 4 and 5 ppm. Only one signal was observed at 6.0 ppm in the region of the $-O-CH_2-O-$ protons, indicating that the amine **12** had not reacted at all. The nitroarene conversion was complete, as indicated by the TLC analysis of the solution and the CH_2Cl_2 washings. The formation of **13** and the absence of the quinolone derived from **12** have also been proved by the analysis of the EI mass spectra of the products of the reaction.

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