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One-pot synthesis of aniline derivatives from nitroarenes under mild conditions promoted by a recyclable polymer-supported palladium catalyst

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1. Introduction

Amines and their derivates act as important synthones in organic chemistry [1]. They are highly versatile building blocks for various organic target molecules and are essential precursors to a variety of biologically active compounds [2], such as pharmaceuticals and agrochemicals. Due to their importance, several methods have been developed for the preparation of amines [3–5]. Direct reductive amination of aldehydes and ketones, in which a mixture of an aldehyde or ketone and an amine is treated with a reductant is one of the most useful methods for the preparation of secondary or tertiary amines [6–9]. The commonest reducing agents are hydrides [10–15], such as, for example, sodium cyanoborohydride and sodium triacetoxyborohydride [16,17] or molecular hydrogen in the presence of a platinum-triad catalyst [9,18,19].

The use of sodium cyanoborohydride and sodium triacetoxyborohydride has as drawback the formation of toxic byproducts (HCN, NaCN) or the use of corrosive acetic acid. A variant of this method consists in the use of organosilanes as reducing reagent [20].

Recently, efforts have been made to carry out the reductive amination of carbonyl compounds directly with nitrobenzene [21,22]. The most commonly used catalytic systems are based on Pd/C with: (i) decaborane at high temperature in the presence of acetic acid to prevent reductive etherification [23]; (ii) HCOONH₄ as hydro-

ABSTRACT

This work describes the one-pot direct reductive amination of carbonyl compounds with nitroarenes promoted by a polymer supported palladium catalyst, in the presence of molecular hydrogen as the reductant. This methodology is applicable, with slight differences, to both aliphatic and aromatic aldehydes. The operational simplicity, the mild reaction conditions, the high yields and the good recyclability of the supported catalyst are major advantages of this method. TEM observations of the catalyst showed that the active species are palladium nanoparticles having a size distribution centered at 5 nm within the polymeric support.

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gen donor at room temperature (only for aliphatic aldehydes) [24]; (iii) molecular hydrogen with aromatic [25] and aliphatic [26] aldehydes as reagents. In the case of aromatic aldehydes, the reaction was carried out stepwise and the imine formation was achieved in more than 24 h. Moreover, for some substrates the use of triethylamine was necessary to poison the catalyst and improve selectivity. With aliphatic aldehydes, high yields were achieved when all the reagents were mixed from the beginning. More recently, Sreedhar et al. reported on gum acacia supported palladium nanoparticles which promoted reductive N-alkylation of nitroarenes using molecular hydrogen as reductant and methanol as solvent [27]. The catalyst was recovered at the end of reaction and recycled up to five runs without loss of activity and selectivity.

Following our studies on the palladium catalyzed hydrogenation reaction [28] of alkenes, alkynes, carbonyl compounds, nitroarenes and nitriles, herein we report the catalytic activity of polymer supported Pd nanoparticles in the direct reductive amination of aldehydes with nitroarenes under atmospheric pressure of hydrogen for the synthesis of mono N-alkyl amines.

2. Experimental

2.1. General considerations

Methanol and nitrobenzene were distilled under inert atmosphere before use. All other chemicals were purchased from commercial sources and used as received. Palladium content in Pdpol was assessed after sample mineralization by atomic absorption spectrometry using a PerkinElmer 3110 instrument. GC–MS data

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(EI, 70 eV) were acquired on a HP 7890 instrument using a HP-5MS cross-linked 5% PH ME siloxane ($30.0 \text{ m} \times 0.25 \text{ mm} \times 0.25 \mu \text{m}$) capillary column coupled with a mass spectrometer HP 5973. The products were identified by comparison of their GC-MS features with those of authentic samples or by their NMR ¹H and ¹³C spectra. Reactions were monitored by TLC carried out on 0.25 mm silica gel coated glass plates using UV light as visualizing agent or by GC-MS. Products were purified by flash column chromatography with silica gel and petroleum ether bp 40-60 °C/dichloromethane as eluant. The microstructure of the polymeric matrix embedded Pd nanoparticles was determined by TEM observations at acceleration voltage of 200 kV (Model JEM 2010, Jeol, Akishima Tokyo, Japan), equipped with X-ray energy dispersive spectroscopy (EDS). The samples were prepared by dispersing the powders in distilled water using an ultrasonic stirrer and then placing a drop of suspension on a copper grid covered with a transparent polymer film, followed by drying and carbon coating. The particle size distributions were obtained by TEM image analysis using the Image] software (freeware software: http://rsb.info.nih.gov/ij/).

2.2. Catalyst preparation

The supported catalyst (Pd-pol) was prepared as described below with slight differences respect to the procedure reported in our previous article [29]. This new procedure used a lower polymerization temperature, in order to prevent the thermal reduction of Pd, which could decrease the catalytic performance of the insoluble material.

221.6 mg (1.25 mmol) of $PdCl_2$ and 175.4 mg (3.0 mmol) of NaCl were placed into a reaction flask and 10 mL of deionized water was added. The resulting brown suspension was stirred for 30 min at 50 °C and during this time, it was converted into a brick red solution (solution A), which was cooled to room temperature.

To a solution of NaOH (200 mg, 5.0 mmol) in water (10 mL), 2-(acetoacetoxy)ethyl methacrylate (HAAEMA) (1.071 g, 5.0 mmol) was added and left under stirring at room temperature for 5 min. The resulting solution was added to the Na₂PdCl₄ solution A at room temperature, causing the sudden precipitation of a red oil. After 40 min stirring, the supernatant solution was removed and the red oil was washed with water (3×5 mL), extracted with methylene chloride (15 mL) and dried over Na₂SO₄. After filtration, the methylene chloride was removed under vacuum and the resulting oil was dissolved in cold THF (3 mL). This solution was treated under stirring with cold pentane (25 mL) affording Pd(AAEMA)₂ as an orange powder, which was washed (2×5 mL) with cold pentane and dried under vacuum for 2 h. Anal. Calc. for PdC₂₀H₂₆O₁₀: C, 45.00; H, 4.92; Pd, 19.97. Found: C, 44.50; H, 4.99; Pd, 19.76. Yield: 90%.

Ethyl methacrylate (2.84g, 25 mmol) was added to a solution containing Pd(AAEMA)₂ (532.8 mg, 1.0 mmol) in THF (3 mL) and the resulting orange solution was warmed up to 50 °C. Then, ethylene glycol dimethacrylate (0.8 mL, 4.24 mmol) and azaisobutyronitrile (5 mg) were added to the solution followed by stirring at $50 \,^{\circ}\text{C}$ exposing it to the light of a table lamp. After 1 h, it was noticed that the stirring was stopped by the formation of the polymer. The mixture was then cooled at room temperature, and 20 mL of acetone was added to the solid obtained. After removal of the solvent, the solid was ground with a mortar and pestle, and left under vigorous stirring in acetone (20 mL) overnight in order to obtain a fine powder. The solid was then washed with acetone $(3 \times 5 \text{ mL})$ and *n*-hexane $(3 \times 5 \text{ mL})$ and dried under vacuum to afford military green powder of Pd-pol. Yield: 3.50 g of polymer. Anal.: C, 52.42%; H, 7.06%; Pd, 2.50%. IR (KBr): $(cm^{-1}) \nu = 2960 \text{ vs}$, 1724 vs, 1605 w, 1506 w, 1481 m, 1266 s, 1145 s, 1025 m.

2.3. Typical experimental procedure for the reductive amination of aromatic aldehydes with nitroarenes (one-pot, two step method)

The catalyst Pd-pol (80 mg, 0.9 mol%) was added to a stirred solution of nitroarene (2.0 mmol) in methanol (2.0 mL). The resulting suspension was stirred under an atmosphere of hydrogen (rubber balloon) at room temperature for the specified period of time (*step 1*). During this time the catalyst turned black. Aldehyde (2.0 mmol) was then added, and the reaction mixture was stirred under air for a couple of minutes, before being stirred under an atmosphere of hydrogen for the specified period (*step 2*). The progress of the reaction was monitored by TLC or/and GC–MS. At the end of reaction, the reaction mixture was filtered and the solvent was removed under reduced pressure to give the crude product, which was purified by flash chromatography using petroleum ether-dichloromethane as eluant.

2.4. Typical experimental procedure for the reductive amination of aliphatic aldehydes with nitroarenes (one-pot, one step method)

The catalyst Pd-pol (80 mg, 0.9 mol%), the nitroarene (2.0 mmol) and the aldehyde (2.0 mmol) were put into a 100 mL Schlenk tube and methanol (2.0 mL) was added. The resulting suspension was stirred under an atmosphere of hydrogen (rubber balloon) at room temperature for the specified period of time. During this time the catalyst turned black. The progress of the reaction was monitored by TLC or/and GC–MS. At the end of reaction, the reaction mixture was filtered and the solvent was removed under reduced pressure to give the crude product, which was purified by flash chromatography using petroleum ether-dichloromethane as eluant.

2.5. Recycling of catalyst

After completion of the reaction the catalyst was recovered by filtration and washed with methanol $(3 \times 5 \text{ mL})$ and diethyl ether $(3 \times 5 \text{ mL})$ and dried under vacuum for further reuse.

3. Results and discussion

The catalyst used in this work is the polymer supported Pd complex (*Pd-pol*) obtained by co-polymerization of $Pd(AAEMA)_2$ (AAEMA⁻ = deprotonated form of 2-(acetoacetoxy)ethyl methacrylate) with ethyl methacrylate and ethylene glycol dimethacrylate [29–32].

An initial evaluation of the catalyst performance was carried for the system benzaldehyde/nitrobenzene under an atmospheric pressure of hydrogen at room temperature in methanol using a PhCHO/PhNO₂/Pd molar ratio of 1/1/0.009.

The use of an aromatic aldehyde as substrate is a tough task as: (a) the hydrogenation to the corresponding alcohol is competitive with the desired reduction of nitrobenzene precluding the formation of the imine intermediate; (b) since the corresponding imine intermediate is quite stable, it can undergo backward reaction to aldehyde and amine, with possible subsequent aldehyde hydrogenation; (c) the target secondary benzyl amine may be decomposed by the Pd catalyst under hydrogen via cleavage of the benzyl group [33].

Optimization of the experimental conditions led to one-pot reaction with 95% yield (Scheme 1). These conditions (*two step method*) involve the following procedure: the initial quantitative reduction of nitrobenzene with hydrogen (1 atm) in the presence of Pd-pol (*step 1*); the addition of benzaldehyde and the subsequent hydrogenation of the resulting imine under one atmosphere



Fig. 1. Reductive amination of benzaldehyde with nitrobenzene over eight cycles.

4

5

6

7

8

1 2 3

cycle

of hydrogen (*step 2*). Blank tests revealed that no product formed when the reaction was carried out in the absence of the Pd catalyst.

As reported by Sreedhar et al., when the reductive amination of benzaldehyde with nitrobenzene was performed in the presence of traditional heterogeneous catalysts, such as $Pd-SiO_2$ and $Pd-TiO_2$, the nitrobenzene was reduced to the corresponding amine moderately, but the hydrogenation of *in situ* generated imine did not proceed even after 24 h [27]. On the other hand, using 10% Pd/C as catalyst, the same reaction gave, after 6 h, only 20% yield of product [27].

Fig. 1 shows the recyclability of the catalyst for the one-pot, two step synthesis of benzyl phenyl amine. In fact Pd-pol could be recovered after reaction (the overall one-pot transformation took 8 h for each cycle) by simple filtration in air and reused several times without loss of activity.

Table 1 shows the results obtained for reactions carried using benzaldehyde or 2-methyl-benzaldehyde and different nitrobenzenes. Very good yields were achieved for the nitrobenzene/2-methylbenzaldehyde system, both in the first run and in the recycle (entries 1–2). Similar results were obtained using *p*-ethyl-nitrobenzene (having an electron donor substituent) as nitro-substrate (entries 3–4). When the dinitro substrate 2,4-dinitrotoluene was used with two equivalents of benzaldehyde, N¹,N³-dibenzyl-4-methylbenzene-1,3-diamine was obtained in

70% yield (entry 5), the main by-products being an isomeric mixture of N¹-benzyl-N³-benzylidene-4-methylbenzene-1,3-diamine and N³-benzyl-N¹-benzylidene-4-methylbenzene-1,3-diamine. While in all other cases the time required to complete step 1 was 5.5 h and that to complete step 2 was 2.5-7 h, the reaction involving 2,4-dinitrotoluene and benzaldehyde required 15 h for step 1 and 26 h for step 2. When p-chloronitrobenzene and benzaldehyde were used, extensive dehalogenation of the nitro compound during step 1 occurred resulting in a yield of phenylbenzylamine as high as 82% (entry 6). In the reaction of *p*-nitroacetophenone with benzaldehyde, high yields in the desired secondary amine containing the carbonyl group were achieved both in the first cycle (entry 7) and in the re-cycle (entry 8). In this case care must be taken in controlling the time of the first step (nitro group hydrogenation) since, once all p-nitroacetophenone is transformed into p-aminoacetophenone the catalyst is able to reduce the carbonyl group to alcohol (and eventually to alkane).

The substrates 5-methyl-2-nitro-phenol and benzaldehyde gave quantitatively the corresponding secondary amine both in the first cycle (entry 9) and in the re-cycle (entry 10).

Aliphatic aldehydes were also used for the one-pot reductive amination with Pd-Pol. In some cases it was not necessary to separate the nitrobenzene reduction step from the imine hydrogenation step. In fact, the aliphatic imine intermediates are readily hydrogenated to the product, and the hydrogenation of the carbonyl group is not competitive with the reduction of the nitro or imine groups. Thus, the reaction of nitrobenzene and *iso*-butyraldehyde gave 83% isolated yield of the desired product after 7.5 h (Scheme 2 and entry 1 of Table 2). The catalyst did not lose activity when recycled (entry 2 of Table 2).

Table 2 also shows results obtained using nitrobenzene with several aliphatic aldehydes. Pivalaldehyde and *iso*-valeraldehyde gave acceptable (72–77%) yields of the desired secondary amines, both in the first run and in the recycle (entries 3–6 of Table 2). 2-Phenylpropanal and phenylacetaldehyde, both having a phenyl group in α position gave lower yields (48–65%, entries 7, 8, 10, 11 of Table 2) due to partial reduction of the aldehyde to alcohol. However, carrying out the reactions with 2-phenylpropanal or phenylacetaldehyde by *two step method* the yield increased to 87% (entry 9 of Table 2) and 90% (entry 12 of Table 2), respectively. The linear aldehyde *n*-heptanal gave poor yield in heptyl phenyl amine when the experiment was carried out by mixing nitrobenzene and *n*-heptanal under H₂ at the beginning of the reaction. By carrying out the same reaction under *two step method*, a satisfactory 80% yield was obtained (entry 13 of Table 2).

We investigated the nature of the catalysis (homogeneous or heterogeneous) by measuring the Pd leaching in solution and by testing the catalytic activity of the mother liquors. In all reported cases, the elemental analyses carried out on the catalyst before and after two catalytic cycles (eight runs for the reaction described in Fig. 1) revealed that the metal content in the catalyst was equal to that of the pristine material. Moreover, the Pd analysis of the reaction solutions after Pd-pol filtration revealed the absence of metal. Finally, to confirm the heterogeneous nature of the catalysis, we isolated the mother liquors of the reaction carried out



Scheme 2. Synthesis of phenyl i-butyl amine.

Table 1One-pot, two step synthesis of aryl-benzyl aminesa.

Entry	Nitroarene	Aldehyde	Product	Time of step 2	Yield ^b (%)
1	PhNO ₂	O H		5 h	95
2 ^c	"	"	"	5 h	93
3	NO ₂	O H		2.5 h	93
4 ^c	"	33	"	2.5 h	95
5	NO2 NO2	O H	H HN	26 h ^d	70 ^e
6	NO ₂	O H	N H	2.5 h	82
7 ^f	NO ₂	O H	N H	2.5 h	96
8 ^{c,f}	" NOs	33	"	2.5 h	95
9f	но	O H	HO	2 h	99 ^e
10 ^{c,f}	, ,,	"	n	2 h	99 ^e

^a Reaction conditions: nitroarene (2.0 mmol), aldehyde (2.0 mmol), methanol (2.0 mL), Pd-pol (0.9 mol%) at room temperature under H₂ (*p* = 1 atm); the time for *step 1* was 5.5 h.

^b isolated yield.

^c recycle of the previous run.

^d the time required to complete *step 1* was 15 h.

^e chromatographic yield.

^f solvent: a mixture of methanol (2.0 mL) and dichloromethane (2.0 mL).

using nitrobenzene and benzaldehyde, stopped at ca. 30% and ca. 60% conversion of the benzylidenephenylimine, by filtration of the supported catalyst after 0.5 h and 1 h from the addition of benzaldehyde, respectively. Then the mixture deprived of Pd-pol was stirred at RT under H₂ (p = 1 atm) for 18 h. GLC analysis of the resulting solution revealed that the imine conversion remained unchanged. In addition, the amount of Pd detected in mother liquors at 30% and 60% imine conversion was negligible (ca. 3 ppm), while the

palladium content in the corresponding recovered catalyst was practically that of the fresh catalyst, within the experimental error.

All these data indicate that Pd leaching during reaction is negligible and that the reaction presumably occurs on the solid surface of the catalyst.

In order to gain insights into the morphology of the polymeric catalyst, TEM analyses were carried out on Pd-pol (i) as pristine (*Pd-pol0*); (ii) after two cycles of reaction with nitrobenzene and

Table 2One-pot, one step synthesis of phenyl-alkylaminesa.

Entry	Aldehyde	Product	Time	Yield ^b (%)
1	O H		7.5 h	83
2 ^c	" О	"	7.5 h	85
3	Н		9 h	77
4 ^c	"	"	9.5 h	75
5	O H		5 h	75
6 ^c	"	"	5.5 h	72
7			9 h	60
8 ^c 9	"	"	9 h 13 h^d	65 87
10	O H		12 h	48
11 ^c 12	"	"	12 h 10 h ^e	50 90
13		H N	8.5 h ^f	80

^a Reaction conditions: nitrobenzene (2.0 mmol), aldehyde (2.0 mmol), methanol (2.0 mL), Pd-pol (0.9 mol%) at room temperature under H₂ (p = 1 atm).

^b isolated yield.

^c recycle of the previous run.

^d carried out using two step method: 6 h for step 1 and 7 h for step 2.

^e carried out using *two step method*: 6 h for *step 1* and 4 h for *step 2*.

^f carried out using two step method: 6 h for step 1 and 2.5 h for step 2.

benzaldehyde (*Pd-pol2*); (iii) after eight cycles of the same reaction (*Pd-pol8*). The corresponding TEM nanostructures are reported in Fig. 2.

TEM image of *Pd-pol0* (Fig. 2a) shows that Pd nanoparticles are round irregular polyhedra with a mean diameter of roughly 9 nm embedded in a smooth microstructure of the polymeric matrix. TEM selected area electron diffraction (SAED) pattern apparently consists of a ring pattern due to the diffraction of the thin metallic Pd-crystallites (inset of Fig. 2a). *Pd-pol0* is found to be constituted by atomic Pd(II) polymeric network. However, the formation in the pristine catalyst of metallic Pd nanoparticles with a low number density and a mean diameter of 9 nm could occur during the thermal polymerization step of the catalyst synthetic procedure. In fact, the formation of primary Pd nanoparticles is caused by thermal decomposition of metal- containing precursors in accordance with the simulated process proposed by Rozenberg et al. [34].

TEM image of *Pd-pol2* (Fig. 2b) shows a higher number of Pd nanoparticles per unit area with respect to the pristine catalyst. The Pd nanoparticles have a bimodal size distribution: the first one centered around 5 nm and the second one describing the small amount of agglomerates. The SAED pattern (inset of Fig. 2b) shows spots and rings typical for agglomerated and nano-crystalline mate-

rial, respectively. In the case of *Pd-pol2* the formation of new Pd nanoparticles is generated by the hydrogen atmosphere [35] under which the two reaction cycles are carried out. In addition, in *Pd-pol2* (Fig. 2b) a rougher surface microstructure of the polymeric matrix is noticed when compared to *Pd-pol0*.

TEM image of *Pd-pol8* (Fig. 2c) shows an even higher number of Pd nanoparticles per unit area with respect to the previous two specimens, but the overall amount of Pd agglomerates remains still small. This explains why the catalytic activity of the supported catalyst recovered after eight cycles was comparable to that of the catalyst employed in two runs.

In conclusion, in all of the three samples the Pd nanoparticle distribution tends to homogeneously distribute within the polymer matrix. For *Pd-pol0* the Pd nanoparticle formation is limited and ascribable only to thermal polymerization of metal containing acrylate-type monomers leading to an average particle size of ca. 9 nm [34]. On the contrary, for *Pd-pol2* and *Pd-pol8* the extensive Pd nanoparticle formation is ascribable to the hydrogen reduction of Pd(II) supported polymer in which spherical Pd nanoparticles with size of ca. 5 nm are obtained [35].

As it was observed for *Pd-pol2*, TEM microstructure of the Pd supported catalyst recovered after two cycles in the reaction between *iso*-butyraldehyde and nitrobenzene



Fig. 2. Transmission electron micrograph and associated SAED pattern and size distribution (insets) of matrix polymer embedded Pd nanoparticles: (a) Pd-pol before use in catalysis (*Pd-pol0*), (b) Pd-pol recovered after two cycles of the reaction described in Fig. 1 (*Pd-pol2*), (c) Pd-pol recovered after eight cycles of the reaction described in Fig. 1 (*Pd-pol2*), (c) Pd-pol recovered after eight cycles of the reaction described in Fig. 1 (*Pd-pol2*).

showed Pd nanoparticles with a size distribution centered at 5 nm.

4. Conclusion

Pd-pol was shown to be an active and reusable catalyst for the one-pot synthesis of secondary amines via reductive amination at room temperature under an atmospheric pressure of H₂. This protocol, applied with slight differences when reacting aromatic aldehydes instead of aliphatic ones, permits the preparation of a diverse range of N-alkyl amines in good yields. Chemical and TEM analyses showed that the catalytically active species are supported Pd nanoparticles with a primary particles' size distribution centered around 5 nm formed under reaction conditions.

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