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Highly regioselective synthesis of *N*-acyl-2,3-dihydropyrrole or *N*-sulfonyl-2,3-dihydropyrrole derivatives by nano-palladium catalyzed cycloisomerization of 1,6-dienes

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ABSTRACT

Porous palladium nanoparticles were prepared using a solution-phase approach. Their structures and shapes were analyzed by XRD, EDS, TEM and HRTEM. These palladium nanoparticles were used to catalyze the cycloisomerization reaction of *N*,*N*-diallylamide or *N*,*N*-diallylsulfonamide, and *N*-acyl-2,3-dihydropyrrole or *N*-sulfonyl-2,3-dihydropyrrole derivatives were therefore synthesized with very high regioselectivity and in good yields. The nano-palladium catalyst showed high efficiency and it can be reused several times. A hydropalladation mechanism was proposed for this reaction.

1. Introduction

The synthesis of polysubstituted pyrroles remains an attractive goal as they occur in biological, pharmaceutical and organic chemistry [1,2]. *N*-acyl-2,3-dihydropyrroles can be prepared from *N*-formylpyrrolidine by anodic methoxylation and subsequent elimination of methanol [3]. These compounds were also synthesized by the isomerization of *N*-acyl-2,5-dihydropyrroles, utilizing $HRhCO(PPh_3)_3$ or $Fe(CO)_5$ as catalysts [4]. A palladium catalyzed isomerization of the corresponding *N*-acyl-2,5-dihydropyrroles to *N*-acyl-2,3-dihydropyrroles was reported. In this procedure, a phosphoric ligand dppp had been used [5].

Transition metal-catalyzed cyclization reactions of unsaturated substrates constitute a powerful and atom economic route for the construction of five-membered ring systems in recent years [6–10]. The alternative synthetic strategy starting from dienes (A) would seem to hold interesting potential as several catalyst systems based on Ni [11–14], Pd [15–18], Pt [19], Rh [20] and Ru [21–24] were described, forming five-membered ring products B–D through a cycloisomerization (Scheme 1). As that was described in previous report [16], palladium can mediate the formation of B, C and D quite selectively under the appropriate reaction conditions, while other transition metals simply mediate the formation of B selectively.

In recent years, there has been growing interest in the fabrication of transition-metal nanoparticles and their applications in organic reactions especially the formation of carbon–carbon bonds [25–28]. For example, palladium nanoparticles stabilized by tetraalkylammonium salts were obtained and used as heterogeneous catalyst for the Suzuki and Stille cross-coupling reactions [29]. In our previous works, bimetallic hollow palladium–cobalt nanoparticles have been prepared and successfully used to catalyze Sonogashira reaction in aqueous media; cobalt hollow nanospheres were also prepared by a wet chemical method and used to catalyze the Heck reaction and Sonogashira reaction with good results [30–32]. In this work, porous palladium nanospheres were prepared and used to catalyze the cycloisomerization of *N*,*N*-diallylamide or *N*,*N*-diallylsulfonamide and *N*-acyl-2,3-dihydropyrrole or *N*-sulfonyl-2,3-dihydropyrrole derivatives were therefore synthesized with very high regioselectivities and good yields (Scheme 2).

2. Results and discussion

Palladium nanoparticles were prepared using a solution-phase approach. Fig. 1 shows the XRD pattern of the sample prepared by the reaction of hydrazine with $[PdCl_4]^{2-}$ ions using acetone and water as mixed solvents and hexadecylpyridinium chloride as a surfactant. The diffraction peaks in the range of $30 < \theta < 85°$

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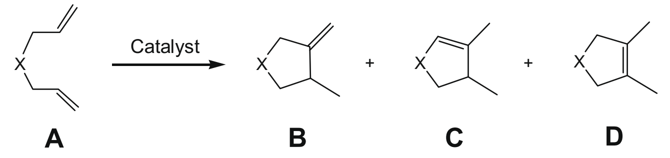
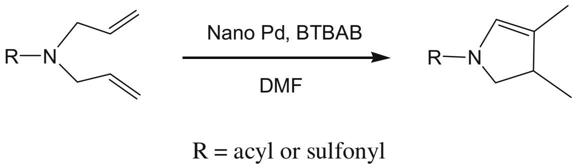


Scheme 1. Cycloisomerization reactions of dienes.



Scheme 2. Nano-palladium catalyzed cycloisomerization of *N*,*N*-diallylamide or *N*,*N*-diallylsulfonamide.

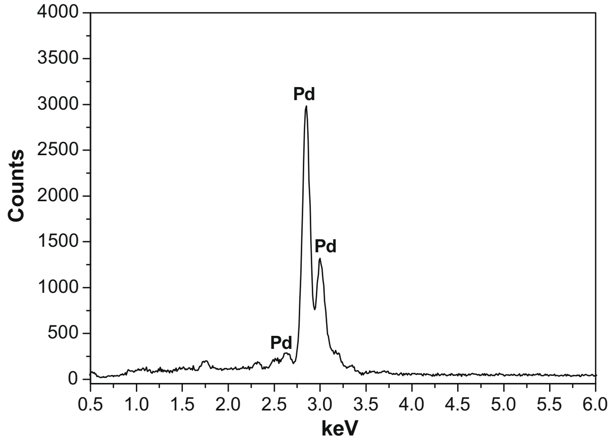


Fig. 2. EDS image of the Pd nanoparticles.

can be indexed as cubic palladium (1 1 1), (2 0 0), (2 2 0) and (3 1 1) and the lattice parameter is $a = 3.90$ Å, which all are in good accordance with the values on the standard card (JCPDS 5-0681). The broader peaks indicate the particles having a small size. EDS analysis (Fig. 2) for the sample shows that they are composed of palladium.

Fig. 3A shows the TEM image of the Pd particles. It can be seen that the particles are of porous spherical shape and the average diameter is about 40 nm mainly ranging from 30 to 50 nm. Further information about the Pd nanoparticles comes from the highly magnified TEM analysis (Fig. 3B). It can be seen from the figure that there are uniform pores with a diameter of about 5 nm on the surface of these Pd nanospheres. Fig. 3C shows the HRTEM image of the Pd nanosphere. It clearly reveals the particles being well crystallized and the lattice fringes with d spacings of about 0.22 nm, which correspond to (1 1 1) reflection of the cubic Pd.

The measured Brunauer–Emmett–Teller (BET) specific surface area for these porous Pd nanospheres, based on nitrogen absorption and desorption isotherm measurements, is 18 $m^2\,g^{-1}$.

Then we tried to use these palladium nanoparticles to catalyze the cycloisomerization of *N*,*N*-diallylamide or *N*,*N*-diallylsulfonamide. It was quite different from the most transition-metal catalyzed cycloisomerization of dienes reported previously which mainly produced the product B (Scheme 1), these palladium nanoparticles catalyzed cycloisomerization giving *N*-acyl-3,4-dimethyl-2,3-dihydropyrrole or *N*-sulfonyl-3,4-dimethyl-2,3-dihydropyrrole (C) as products with very high regioselectivity. For optimizing the reaction conditions, *N*,*N*-diallylbenzamide was chosen as a model reactant. GC–MS and ^{1}H NMR analyses showed that *N*-benzoyl-3,4-dimethyl-2,3-dihydropyrrole (C) was generated with a high yield and no other isomers (B and D) were detected. The experiment showed that 1 mol% of Pd catalyst was sufficient to catalyze the cycloisomerization reaction with a good result. Polar protic solvent such as ethanol was disadvantageous to this reaction. In nonpolar solvent such as toluene, it gave a low yield. In polar aprotic solvent *N*,*N*-dimethylformamide (DMF), it gave the satisfactory yield. At room temperature, the reaction nearly could not proceed. However, the yields improved up to 90% when the reaction was carried out at 70 °C.

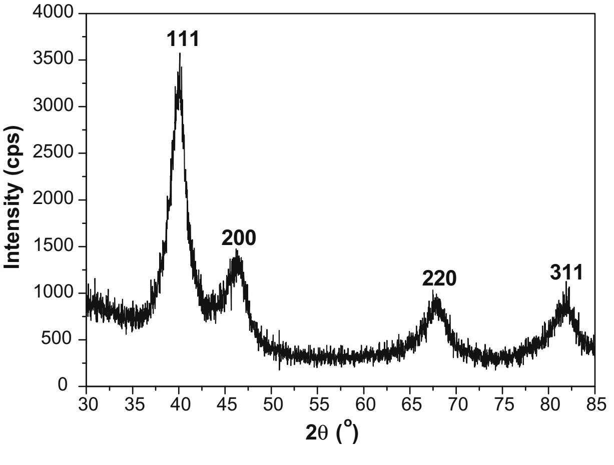


Fig. 1. XRD pattern of Pd nanoparticles prepared by the reaction of hydrazine with $[PdCl_4]^{4-}$ ions using acetone and water as mixed solvents and hexadecylpyridinium chloride as a surfactant.

Stabilizers for metal nanoparticles to prevent their agglomeration were very important in many preparations and applications of nanoparticles [33,34]. Several quaternary ammonium salts (QAS) were therefore tried to be used in this cycloisomerization reaction to stabilize the nano-palladiums and enhance their catalytic capability, and it led to a dramatic improvement of catalytic activity. Among several quaternary ammonium salts or surfactants such as tetra-*n*-butylammonium bromide (TBAB), dodecyltrimethylammonium bromide (DTMAB) and benzyltri-*n*-butylammonium bromide (BTBAB), BTBAB produced the best effect. When the amount of BTBAB reached to 20 mol%, the activity of this catalytic system attained the highest (Table 1).

Under the selected reaction conditions, the reaction of a series of reactants, both *N*,*N*-diallylamides and *N*,*N*-diallylsulfonamides gave the corresponding compounds with very high selectivities. No other isomers, except *N*-acyl-3,4-dimethyl-2,3-dihydropyrrole or *N*-sulfonyl-3,4-dimethyl-2,3-dihydropyrrole were detected, as the reaction of *N*,*N*-diallylbenzamide described above. It was interesting that an even higher activity was observed with *N*,*N*-diallylsulfonamide as substrate (Table 2, entries 1–4). At a lower temperature of 30 °C, and within 4–7 h, the reaction could produce *N*-sulfonyl-3,4-dimethyl-2,3-dihydropyrroles with perfect yields. Both aromatic and aliphatic reactants gave the corresponding cyclization products with good yields, and the substituted groups of aromatic ring with electron donating or withdrawing effect did not affect the reaction obviously.

Another notable advantage with this reaction was the recyclability of the nano-Pd catalyst. The catalyst could be reused after being separated from the solution and washed sufficiently with methanol and ether. After being reused five times, the TEM image showed that the modalities of the Pd nanospheres did not change obviously, and the yield of the cycloisomerization did not reduce