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Article (Dedicated to Professor Yi Chen on the occasion of his 80th birthday)

Synthesis of in-situ surfactant-free Pd nanoparticle catalysts for the synthesis of aromatic azo compounds and for unsaturated bond hydrogenation by hydrogen transfer

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ABSTRACT

We developed a simple and efficient method to synthesize aromatic azos by hydrogen transfer using palladium(II) acetylacetonate as a catalyst and isopropyl alcohol as a hydrogen source. Furthermore, this system also showed catalytic potential for the hydrogenation of carbonyl groups or C=C bonds with yields up to ~97%.

1. Introduction

Hydrogen transfer catalyzed by heterogeneous transition metal complexes has found widespread use in the reduction of organic compounds recently [1–11], and this competes with hydrogenation using molecular hydrogen. The success of this technique is due to its operational simplicity, high selectivity [12–15], and the reduced risks associated with the application of inflammable hydrogen gas. Despite notable achievements over the last few decades, the search for a facile, cost-effective, and environmentally benign procedure that avoids the use of expensive and hazardous transition metals, hazardous complexes or toxic chemicals is of continuing interest to synthetic chemists for different catalytic reductions [9, 11, 16–18].

Aromatic azo compounds, as important industrial products and analytical reagents, have been widely applied in various fields such as drugs, organic dyes, food additives, and materials exhibiting photochemical properties [19–23]. Therefore, the preparation of aromatic azo compounds by an environmentally benign and an industrially applicable process attracts attention [24–27]. The synthesis of azo compounds is often carried out by the reduction of nitroaromatics with lead metal or by the oxidation of anilines from lead tetraacetate [28–30], which involves the frequent use of toxic transition metals. Alternatively, Grirrane et al. [31] introduced a novel method to prepare aromatic azo compounds from aromatic anilines in the presence of Au-based catalysts under 5 atm of oxygen pressure. Moreover, they also demonstrated that the azo compound can be obtained from the corresponding nitroaromatics through a two-step, one-pot reaction by combining the reduction of the

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nitroaromatic and the oxidation of the aniline under 9 atm of hydrogen and 5 atm of oxygen [32]. It is worth mentioning that molecular hydrogen was used as a reducing agent, but it ignites easily and presents considerable hazards, particularly on large scale. Herein, we report aromatic azo formation by a transfer reduction process using hydrogen donors. This process has real and potential advantages such as the absence of gas containment and pressure vessels, and simple solution agitation.

Pd catalysts play an important role in hydrogenation and coupling reactions in organic synthesis. Novel catalysts such as Pd-based nanomaterials [26, 33–37] or surfactant-free systems with higher catalytic activity have emerged recently. For example, surfactant-free $PdCl_2$ catalyzes the Suzuki coupling reaction in water [38], palladium(II) acetate ($Pd(OAc)_2$) works as a highly active catalyst for the Heck reactions of aryl chlorides in the absence of an organic ligand [39], and surfactant-free $Pd(OAc)_2$ promotes the direct arylation of furans in high yield [40]. Inspired by these studies, we used a surfactant-free Pd catalyst to synthesize both symmetric and asymmetric azo compounds from a wide range of substituted nitroaromatics and through a one-step reductive reaction. We obtained the target azo compounds in good to excellent yields. In addition, our system is also highly efficient for the catalytic hydrogenation of different unsaturated bonds in the presence of a C=O and C=C bonds under the same mild conditions. We expect that the surfactant-free Pd-catalyzed transfer hydrogenation system can be widely used to synthesize valuable azo compounds, alcohols, and saturated compounds.

2. Experimental

2.1. General

The aromatic nitro compounds were purchased from Sinopharm Chemical Reagent Co. Ltd. Palladium(II) acetylacetonate ($Pd(acac)_2$) was purchased from Sino-platinum Metal Co. Ltd. All materials were used without further purification. Transmission electron microscopy (TEM) measurements were conducted using a JEOL JEM-200CX instrument at an accelerating voltage of 200 kV. The product mixtures were analyzed by GC (VARIAN CP-3800 GC, HP-5 capillary column, FID detector) and GC-MS (VARIAN 450-GC & VARIAN 240-GC) equipped with a CP8944 capillary column (30 m × 0.25 mm) and an FID detector. The NMR spectra were measured on a spectrometer at 400 MHz for ^1H and 100 MHz for ^{13}C in $CDCl_3$ solution.

2.2. Typical catalytic transfer hydrogenation procedure

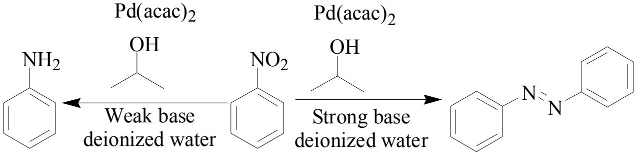
To a reaction tube equipped with a magnetic stirrer an appropriate amount of $Pd(acac)_2$ (2–3 mg), KOH (112 mg, 2 mmol), nitrobenzene (102 μL, 1 mmol), isopropyl alcohol (2 mL), and deionized water (0.25 mL) were added. The air in the tube was then exchanged 3 times with 1 atm of N_2. Finally, the tube was immersed in an oil bath at 100 °C in a sealed N_2 system. After stirring for 24 h at 100 °C, the mixture was cooled to room temperature. A sample of the mixture was immediately analyzed by GC and GC-MS.

3. Results and discussion

To find optimal conditions for the reductive coupling reaction, we used nitrobenzene as the model substrate to test the effect of different bases on the catalytic activity and selectivity of our system. This consists of 1 mmol nitrobenzene, 5–6 mg $Pd(acac)_2$ as catalyst, 2 mL isopropyl alcohol as a hydrogen donor, and 0.25 mL deionized water as solvent. As shown in Table 1, aniline was the only product found when using the weak bases K_2CO_3 or $(C_2H_5)_3N$, and the conversion was less than 5%. $(CH_3)_3COK$ (Table 1, entry 6) gave a high yield for the catalytic conversion at the same base concentration, but it had a relatively low selectivity for the generation of azobenzene compared with NaOH (Table 1, entry 3) or KOH (Table 1, entry 5). Considering the relatively higher price and larger molecular weight of $(CH_3)_3COK$, NaOH or KOH are more suitable for industrial application. We found that an increase in the ratio of KOH in the mixture increased the conversion and selectivity (Table 2). The yield of azobenzene increased and was 86.7% when 4 equivalents of KOH were used (Table 2, entry 4).

A photograph of azobenzene formation is shown in Fig. 1. The clear yellow solution turned dark brown after 18 h of reac-

Table 1
Effect of bases on the nitrobenzene coupling reaction.



Entry	Base	Conversion [a] (%)	Selectivity [a] (%)		
			Azo-	Azoxy-	Aniline
1	K_2CO_3	4.9	—	—	100
2	$(C_2H_5)_3N$	0.8	—	—	100
3	NaOH	19.4	8.5	86.0	5.5
4[b]	KOH	> 99	86.7	—	13.3
5	KOH	57.2	14.8	75.0	10.2
6	$(CH_3)_3COK$	92.7	5.7	87.2	7.1

Reactions condiction: $Pd(acac)_2$ catalyst 5–6 mg, nitrobenzene 1 mmol, base 1 mmol, isopropyl alcohol 2 mL, deionized water 0.25 mL, 100 °C, 18 h. [a] GC result. [b] 4 mmol base.

Table 2
Azobenzene formation from nitrobenzene using different amounts of KOH and H_2O.

Entry	*t* (h)	*i*-PrOH (mL)	H_2O (mL)	KOH (mmol)	Conversion [a] (%)	Selectivity [a] (%)		
						Azo-	Azoxy-	Aniline
1	12	2	0.25	4	> 99	44.6	34.2	21.2
2	18	2	0.10	4	> 99	75.3	—	24.7
3	18	2	0.20	4	100	77.0	—	23.0
4	18	2	0.25	4	> 99	86.7	—	13.3
5	18	2	0.50	4	> 99	84.6	—	15.4
6	18	2	0.75	4	> 99	51.0	34.8	14.2
7	18	2	1.00	4	> 99	26.6	51.2	22.2
8	24	2	0.25	4	100	84.4	—	15.6
9	18	2	—	4	100	48.4	—	51.6
10	18	2	0.25	1	57.2	14.8	75.0	10.2
11	18	2	0.25	2	> 99	12.4	81.1	6.5
12	18	2	0.25	3	> 99	50.4	39.3	10.3
13	18	2	0.25	5	100	38.5	52.1	9.4

Reaction conditions: $Pd(acac)_2$ catalyst 5–6 mg, nitrobenzene 1 mmol, isopropyl alcohol 2 mL, deionized water little, 100 °C. [a] GC result.