Selective synthesis of *N*-aryl hydroxylamines by the hydrogenation of nitroaromatics using supported platinum catalysts†

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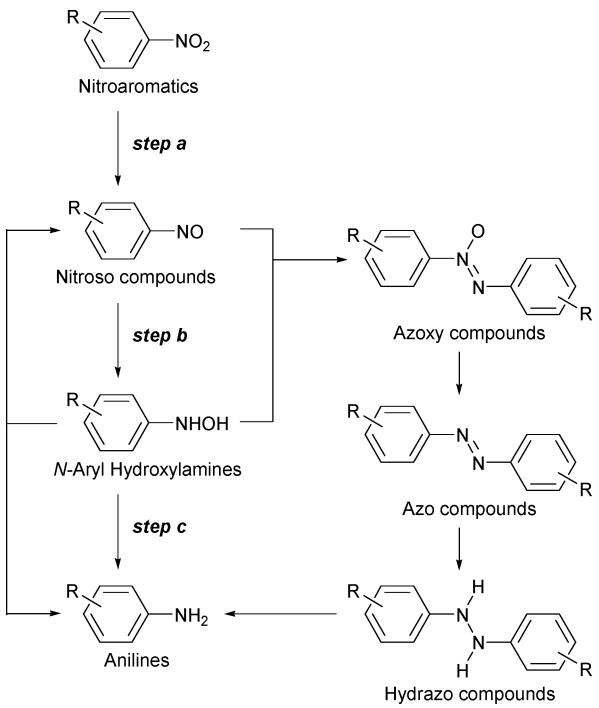
Various substituted nitroaromatics were successfully hydrogenated to the corresponding *N*-aryl hydroxylamines in excellent yields (up to 99%) using supported platinum catalysts such as Pt/SiO_2 under a hydrogen atmosphere (1 bar) at room temperature. The key to the fast and highly selective formation of hydroxylamines is the addition of small amounts of amines such as triethylamine and dimethyl sulfoxide; amines promote the conversion of nitroaromatics, while dimethyl sulfoxide inhibits further hydrogenation of hydroxylamines to anilines. The promotive effect depends on which type of amine and primary amine was most effective. The hydrogenation efficiently proceeded in common organic solvents, including isopropanol, diethyl ether, and acetone. This methodology should extend the application range of conventional solid catalysts to fine chemicals synthesis.

Introduction

Organic hydroxylamines are useful compounds in a wide variety of applications, including intermediates in the synthesis of biologically active substances,[1] reagents for organic synthesis,[2] and raw materials for a polymerization inhibitor.[3] Hydroxylamines have been synthesized *via* various methods; examples include reactions of alkyl or aryl halides with hydroxylamine,[4] reduction of nitro compounds using a stoichiometric reductant such as zinc or tin,[5] reduction of nitro or oxime compounds with boron hydrides,[6] reduction of nitro compounds with hydrazine using a rhodium complex catalyst,[7] and biosynthesis using bakers' yeast.[8] However, these processes are not necessarily environmentally benign and economically beneficial. In addition, some of them are disadvantageous in terms of scaling up and industrial applications.

Selective catalytic hydrogenation of nitro compounds is an ideal process to produce hydroxylamines because hydrogen is a relatively cheap reductant and the sole by-product is water. However, hydrogenation of a nitro group is a typical consecutive reaction, and reduction using noble metal catalysts usually continues until an amino group is produced (Scheme 1). Actually, hydrogenation of nitroaromatics to manufacture anilines[9] and aminophenols[10] is an industrially important reaction. Furthermore, the condensation of nitroso compounds with hydroxylamines and/or the disproportionation of hydroxylamines could concur with the successive reduction of nitro compounds.[11] Therefore, it is very difficult to obtain hydroxylamines in high yields, and there have been few reports on the selective formation of hydroxylamines *via* hydrogenation.[12–14]



Scheme 1 Proposed reaction pathways for the hydrogenation of nitroaromatics.

In his pioneering work, Rylander found that dimethyl sulfoxide (DMSO) works as an additive to effectively increase the selectivity of *N*-phenylhydroxylamine (PHA) during the hydrogenation of nitrobenzene (NB) over platinum on a carbon catalyst.[13] However, in his synthetic procedure, it is essential to interrupt the reduction after the absorption of two equivalents of hydrogen, and the addition of DMSO greatly reduces the catalytic activity. Later, Karwa and Rajadhyaksha[14] investigated

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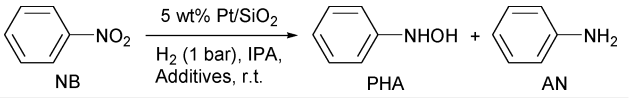
the hydrogenation of NB in the presence of DMSO under high pressure conditions, but the formation of aniline (AN) occurs in parallel with the formation of PHA, and the maximum selectivity of PHA is less than 80%.[14] Thus, the development of more efficient and practical methods to synthesize *N*-aryl hydroxylamines remains a challenge. We recently found that the coexistence of small amounts of amines and DMSO remarkably promotes the formation of *N*-aryl hydroxylamines in the selective hydrogenation of nitroaromatics over supported platinum catalysts. In this paper, we report a highly efficient synthetic method to afford *N*-aryl hydroxylamines in excellent yields (up to 99%) under mild conditions such as atmospheric hydrogen and room temperature.

Results and discussion

Hydrogenation of NB in isopropanol (IPA) under a hydrogen pressure of 1 bar at room temperature using a commercial 5 wt% platinum on silica (Pt/SiO_2) catalyst yielded AN as the major product (Table 1, entry 1). As mentioned in the Introduction, the addition of DMSO to the reaction system improves the selectivity of PHA.[13,14] Indeed, when hydrogenation of NB was conducted under a high hydrogen pressure (10 bar) in the presence of DMSO, PHA was preferentially formed in 73% yield after 5 h (Table 1, entry 2, Fig. 1(a)), which agrees well with the result reported by Karwa and Rajadhyaksha.[14] However, the addition of DMSO significantly decreased the catalytic activity, and under atmospheric hydrogen, the yield of PHA was only 7.2% after 2 h (Table 1, entry 3, Fig. 1(b)).

To increase the productivity of PHA, steps **a** and **b** in Scheme 1 must be accelerated while retarding the progress of step **c**. We envisaged that the presence of an electron-donating compound like an amine might increase the hydride character of hydrogen on platinum[9a] and promote the attack of the activated hydride species to the nitrogen–oxygen bond in NB. Thus, we examined the additive effect of triethylamine (TEA). When small amounts of TEA (0.072 mmol) and DMSO (0.42 mmol) were added to the reaction mixture, the conversion at a reaction time of 2 h dramatically increased from 7.3% to 54.3% (Table 1, entry 4). It should be noted that a high PHA selectivity was maintained. In addition to PHA, the only other hydrogenation product was AN; the formation of nitrosobenzene, azoxybenzene, azobenzene, or hydrazobenzene was not observed. A prolonged reaction time increased the conversion of NB while maintaining a high PHA selectivity (Fig. 1(c)). The PHA yield also increased as the amount of TEA increased, a quantitative yield of PHA was achieved within 2 h when 0.36 mmol of TEA was added (Table 1, entry 5). This PHA yield (99%) is the highest level achieved to date through hydrogenation of NB. However, the addition of TEA alone did not promote the reaction, and AN was mainly produced (Table 1, entry 6), indicating that the coexistence of DMSO and TEA is important for the fast and highly selective formation of PHA. The promotive effect of TEA was also observed for commercial 5 wt% Pt/C and Pt/Al_2O_3 catalysts as well as 5 wt% platinum on silica (Pt/SiO_2 (P)) catalyst prepared in this study, although the optimal reaction conditions to achieve high yields (> 95%) differed among the supports (Table 1, entries 7–9). On the other hand, a commercial 5 wt% Pd/SiO_2 catalyst gave AN as the major product (Table 1, entry 10). Additionally,

Table 1 Selective hydrogenation of nitrobenzene[a]



Entry	Additives (mmol) DMSO	TEA	t (min)	Conv.[b] (%)	Yield (%)[b] PHA	AN	Select.[b] (%)
1	0	0	10	47.1	10.3	36.8	21.9
2[c]	0.42	0	300	97.1	73.2	23.9	75.4
3	0.42	0	120	7.3	7.2	0.1	98.6
4	0.42	0.072	120	54.3	53.9	0.5	99.2
5	0.42	0.36	120	100	98.8	1.2	98.8
6	0	0.072	10	42.3	12.3	30.0	29.1
7[d]	1.26	0.072	120	100	97.2	2.8	97.2
8[e]	1.26	0.072	90	100	96.7	3.3	96.7
9[f]	0.84	0.36	210	98.4	95.0	3.4	96.6
10[g]	0.42	0.36	360	98.1	15.0	83.1	15.3
11[h]	0.42	0.36	720	10.0	9.0	1.0	90.0

[a] Nitrobenzene (NB): 2 mmol, 5 wt% Pt/SiO_2 (Escat™ 2351): 20 mg, H_2: 1 bar, isopropanol (IPA): 2 mL, additives: dimethyl sulfoxide (DMSO) and triethylamine (TEA), room temperature. [b] Determined by HPLC with toluene as an internal standard. [c] H_2: 10 bar. [d] 5 wt% Pt/C: 20 mg. [e] 5 wt% Pt/Al_2O_3: 20 mg. [f] 5 wt% Pt/SiO_2 (P): 20 mg. [g] 5 wt% Pd/SiO_2 (Escat™ 1351): 20 mg. [h] 5 wt% Ru/SiO_2 (P): 20 mg.

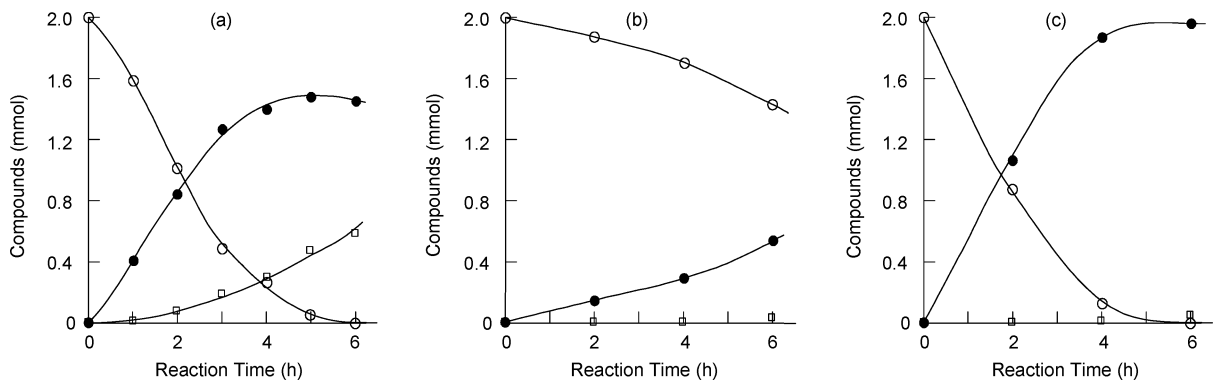
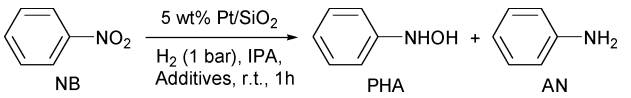


Fig. 1 Reaction profiles for hydrogenation of nitrobenzene (a) under H_2 (10 bar), (b) under H_2 (1 bar), and (c) with triethylamine (0.072 mmol) under H_2 (1 bar). Nitrobenzene (○), *N*-phenylhydroxylamine (●), and aniline (□). Reaction conditions: nitrobenzene (2 mmol), 5 wt% Pt/SiO_2 (Escat™ 2351: 20 mg), isopropanol (2 mL), dimethyl sulfoxide (0.42 mmol), room temperature.

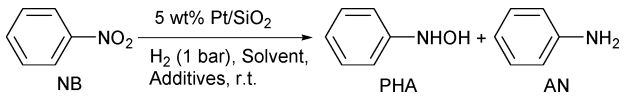
Table 2 Promotive effect of various amine derivatives[a]



Entry	Additive Amines	Conv.[b] (%)	Yield (%)[b] PHA	AN	Select.[b] (%)
1	Et_3N	26.5	26.3	0.2	99.3
2	*iso*-Pr_2NEt	15.4	15.3	0.1	99.5
3	*iso*-Pr_2NH	33.0	32.8	0.2	99.6
4	Et_2NH	55.0	49.8	0.2	99.5
5	Piperidine	71.5	71.0	0.5	99.2
6	*sec*-$BuNH_2$	85.5	84.7	0.8	99.0
7	*n*-$BuNH_2$	78.3	77.5	0.8	99.0
8	$PhCH_2NH_2$	83.0	82.4	0.6	99.4
9	TMEDA	68.3	68.0	0.3	99.6
10	Pyridine	13.5	13.4	0.1	99.5
11	$PhNMe_2$	6.6	6.5	0.1	99.2
12	$[PhCH_2NEt_3]^+Cl^-$	0.5	0.5	0.0	>99.9
13	None	4.1	4.0	0.1	97.6

[a] Nitrobenzene (NB): 2 mmol, 5 wt% Pt/SiO_2 (Escat™ 2351): 20 mg, H_2: 1 bar, isopropanol (IPA): 2 mL, additives (dimethyl sulfoxide: 0.42 mmol, amine: 0.072 mmol), room temperature, 1 hour. [b] Determined by HPLC with toluene as an internal standard. [c] TMEDA: *N*,*N*,*N*′,*N*′-tetramethylethylenediamine.

Table 3 Effect of solvents[a]



Entry	Solvent	t (min)	Conv.[b] (%)	Yield (%)[b] PHA	AN	Select.[b] (%)
1	IPA	105	98.6	97.3	1.3	98.7
2	EtOH	105	96.1	94.6	1.5	98.4
3	Diethyl ether	150	100	98.8	1.2	98.8
4	CH_3CN	210	99.5	98.6	0.9	99.1
5	THF	270	100	99.8	0.2	99.8
6	Ethyl acetate	300	99.2	98.2	1.0	99.0
7	Acetone	375	100	99.5	0.5	99.5
8	CH_2Cl_2	300	94.0	83.9	10.1	89.3
9	Toluene	240	95.6	82.4	13.2	86.2
10	Hexane	480	3.2	3.0	0.2	93.8
11[c]	Et_3N	480	94.5	94.4	0.1	99.9

[a] Nitrobenzene (NB): 2 mmol, 5 wt% Pt/SiO_2 (Escat™ 2351): 20 mg, H_2: 1 bar, solvent: 2 mL, additives (dimethyl sulfoxide: 0.42 mmol, $nBuNH_2$: 0.072 mmol), room temperature. [b] Determined by HPLC with toluene as an internal standard. [c] Dimethyl sulfoxide: 0.42 mmol, $nBuNH_2$: 0 mmol.

the catalytic activity of 5 wt% ruthenium on silica (Ru/SiO_2 (P)) prepared in this study was very low (Table 1, entry 11).

The addition of a variety of amines accelerated the selective hydrogenation of NB to PHA over the Pt/SiO_2 catalyst, but the promotive effect depended on the type of amine. Generally, the effect was in the order of tertiary < secondary < primary (Table 2, entries 1–8). Additionally, diamines such as *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) were more effective than monoamines like TEA (Table 2, entry 9). Diisopropylamines were less effective, possibly due to the larger steric hindrance around the nitrogen atom (Table 2, entries 2 and 3). Moreover, aromatic amines such as pyridine and *N*,*N*-dimethylaniline and quaternary ammonium salts like benzyltrimethylammonium chloride were ineffective.

Furthermore, we investigated the effect of solvents using *n*-$BuNH_2$ as an amine additive. Table 3 compares the reaction time required to achieve a conversion level greater than 90%. Alcoholic solvents such as IPA and ethanol were the most suitable (Table 3, entries 1 and 2). In addition, the reaction efficiently proceeded in common organic solvents, including diethyl ether and acetone, but longer reaction times were required (Table 3, entries 3–7). In contrast, employing dichloromethane or toluene slightly decreased the PHA selectivity, possibly because the amount of DMSO added was insufficient to suppress the formation of AN (Table 3, entries 8 and 9). Non-polar hexane was a poor solvent. Although TEA itself was a good solvent to selectively produce PHA, the catalytic activity decreased.

In organic synthesis, the addition of small amounts of additives to control the performance of conventional solid catalysts is a practical and effective method, especially for fine chemicals synthesis.[15,16] For selective hydrogenation over solid catalysts, there are numerous examples of enhanced regio- and stereoselectivity caused by additives, including organic compounds or metal salts.[16,17] On the other hand, the addition of nitrogen-, phosphorus- or sulfur-containing compounds often leads to poisoning of the catalyst.[9j,18] In the selective hydrogenation of NB over platinum catalysts under pressurized hydrogen (*ca.* 7 bar), for instance, the addition of an ammonia solution improves the selectivity toward PHA, but slightly decreases the catalytic activity.[12e] In this study, small amounts of amines promoted the conversion of NB (steps **a** and **b** in Scheme 1), while DMSO inhibited further hydrogenation to AN (step **c**). That is, the presence of both a promoter and an inhibitor as well as optimizing their amounts are essential to exclusively form PHA.

To elucidate which step, **a** or **b**, in Scheme 1 is promoted by the additional amines, nitrosobenzene was also hydrogenated over the Pt/SiO_2 catalyst. Under these conditions in the presence of DMSO, PHA was the minor product. The major product was azoxybenzene (Fig. 2(a)), which was formed by dehydrative condensation between PHA and nitrosobenzene.[11] On the other hand, the addition of TEA had a negligible effect on the reaction. Moreover, the rate of azoxybenzene formation in the

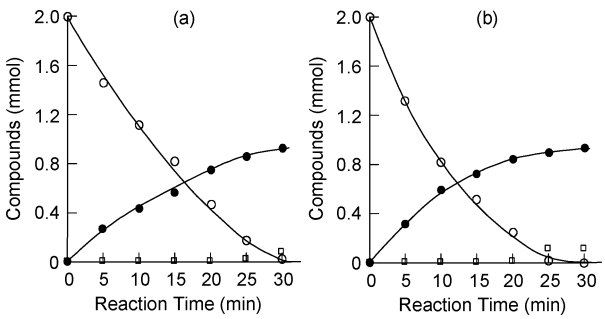


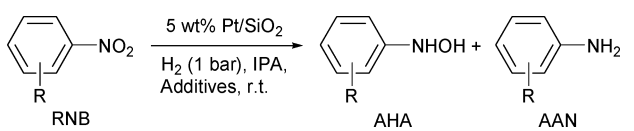
Fig. 2 Reaction profiles for hydrogenation of nitrosobenzene (a) in the absence of triethylamine and (b) in the presence of triethylamine (0.072 mmol). Nitrosobenzene (○), azoxybenzene (●), and *N*-phenylhydroxylamine (□). Reaction conditions: nitrosobenzene (2 mmol), 5 wt% Pt/SiO_2 (Escat™ 2351: 20 mg), H_2 (1 bar), isopropanol (2 mL), dimethyl sulfoxide (0.42 mmol), room temperature.

hydrogenation of nitrosobenzene was much faster than the rate of PHA formation in the hydrogenation of NB. Therefore, it is likely that the additional amines accelerate step **a** in Scheme 1.

For the Pd-catalyzed hydrogenation of *p*-chloronitrobenzene using $SnCl_4$ as a promoter, Li *et al.*[19] have proposed that the Sn^{4+} ion interacts with the oxygen atom of the nitro group to decrease the electron density of nitrogen, which accelerates hydrogenation. In this study, the promotive effect of amines was generally in the order of tertiary < secondary < primary (Table 2). Thus, we hypothesize that the promotive effect of amines is due to the activation of the nitro group by the amine proton, and partly assisted by the increased hydride character of hydrogen on platinum. The coexistence of DMSO is another crucial factor for the promotive effect. The strong adsorption of DMSO on the active sites during hydrogenation may cause weakly adsorbed amines to effectively activate the nitro group instead of acting as a catalytic poison. The reason DMSO inhibits step **c** in Scheme 1 is unclear, but the N-OH moiety of PHA is analogous to the S-OH structure in an imaginary enol type of DMSO. Hence, it is possible that DMSO blocks the adsorption sites on the platinum surface, which are easily accessible to PHA, and prevents successive hydrogenation of PHA.

As summarized in Table 4, our synthetic method successfully hydrogenated various nitroaromatics (RNB) substituted with an electron-withdrawing or an electron-donating group to the corresponding *N*-aryl hydroxylamines (AHA) in excellent yields. Nitroaromatics with electron-donating substituents like a methoxy group required longer reaction times to complete the reaction (Table 4, entry 11). 4-Chloronitrobenzene was selectively hydrogenated to 4-chlorophenyl hydroxylamine without carbon–chlorine bond cleavage (Table 4, entry 3). Interestingly, in the case of nitroaromatics with other reducible functional groups such as nitrile, ester, or vinyl groups, only the nitro moiety was hydrogenated to the hydroxylamino group (Table 4, entries 1, 2 and 7). Furthermore, the Pt/SiO_2 catalyst recovered by filtration from the product solution could be reused although the catalytic activity slightly decreased (Table 4, entry 6).

Table 4 Selective hydrogenation of nitroaromatics[a]



Entry	R	t (min)	Conv.[b] (%)	Yield (%)[b] AHA	AAN	Select.[b] (%)
1	4-CN	95	98	98	<1	>99
2	4-CO_2Me	95	100	>99 (88[c])	<1	>99
3	4-Cl	100	100	98	2	98
4	4-F	100	97	96	1	99
5	H	105	99	98	1	99
			98.6[d]	97.3[d]	1.3[d]	99.7[d]
6[e]	H	115	98.2[d]	97.0[d]	1.2[d]	98.8[d]
7	4-CH=CH_2	180	97	97	3	97
8	4-Me	180	97	97	2	98
9	3-Me	150	98	98	2	98
10	2-Me	300	98	98	2	98
11	4-OMe	300	96	96	3	97

[a] Nitroaromatics (RNB): 2 mmol, 5 wt% Pt/SiO_2 (Escat™ 2351): 20 mg, H_2: 1 bar, isopropanol (IPA): 2 mL, additives (dimethyl sulfoxide: 0.42 mmol, *n*$BuNH_2$: 0.072 mmol), room temperature. [b] Determined by ^{1}H NMR. [c] Isolated yield after silica gel column chromatography. [d] Determined by HPLC with toluene as an internal standard. [e] Recovered catalyst was used.

Conclusions

We have developed a highly efficient synthetic method of *N*-aryl hydroxylamines by selective hydrogenation of nitroaromatics using supported platinum catalysts. Simply adding small amounts of amines and DMSO to the reaction mixture realized the formation of hydroxylamines in excellent yields (up to 99%) under a hydrogen atmosphere (1 bar) at room temperature. This method is applicable to a wide range of substituted nitroaromatics and organic solvents. Thus, we believe that the present methodology will extend the application range of conventional solid catalysts to fine chemicals synthesis.

Experimental

General information

All nitroaromatics, nitrosobenzene, azoxybenzene, amine derivatives, DMSO and solvents were commercial products and were used without further purification. Solvents were degassed with argon babbling for 1 h before being used. Hydrogen (Taiyo Nippon Sanso, G1 grade, 99.99999%) was used without further purification. Argon (Taiyo Nippon Sanso, G1 grade, 99.9999%) was used after purification by passing through a Dryclean column (4A molecular sieves, Nikka Seiko) and a Gasclean CC-XR column (Nikka Seiko). 5 wt% Pt/SiO_2 (BASF/Engelhard, Escat™ 2351) and 5 wt% Pd/SiO_2 (BASF/Engelhard, Escat™ 1351) were obtained from Strem Chemicals and stored in a dry box. 5 wt% Pt/C and 5 wt% Pt/Al_2O_3 were obtained from Sigma-Aldrich and also stored in a dry box. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL-LA400WB superconducting high-resolution spectrometer (400 MHz for ^{1}H). HPLC was carried out on a Shimadzu HPLC system equipped with UV-detector SPD-10A*vp* and Wakosil 5C18 column. IR spectra were measured using a Shimadzu FTIR-8200PC spectrometer.

A typical procedure to selectively hydrogenate nitroaromatics

A typical procedure to selectively hydrogenate nitroaromatics is as follows: 5 wt% Pt/SiO_2 (20 mg) was placed in a glass vessel (25 mL) and reduced in a hydrogen stream (30 mL/min) at 200 °C for 1 h. After cooling to room temperature, the hydrogen stream was replaced by an argon stream. A Teflon-coated magnetic stir bar, solvent (2 mL), DMSO (0–1.26 mmol), amine derivatives (0–0.36 mmol), and nitroaromatics (2 mmol) were successively placed in the vessel, and the suspension was purged with hydrogen. Then, the reaction mixture was stirred (1500 rpm) under 1 bar of hydrogen at room temperature. The stirring rates from 600 to 1500 rpm did not affect the reaction rates. During the reaction, hydrogen was continuously supplied to maintain the pressure (1 bar). The reaction mixture was periodically sampled to determine the conversion and yield by HPLC analysis using toluene as an internal standard. After the reaction, the catalyst was removed by filtration, and the filtrate

was concentrated under reduced pressure. The identity of the hydrogenation products was confirmed by comparing their ^{1}H and ^{13}C NMR spectra to those of authentic samples.

Caution

Most hydroxylamines are quite toxic and cause irritation to the skin or eyes. Contact of hydroxylamines with an oxidizer should be avoided, because they are sometimes used as a strong reducing agent. Additionally, such compounds should be handled with care, because an explosion or fire may occur when heated.

Preparation of 5 wt% Pt/SiO_2 (P) Catalyst

Silica (Fuji Silysia Chemical, CARiACT Q-6, surface area of 560 m^2/g, pore volume of 0.79 cm^3/g) was used as a support. The 5 wt% platinum on silica catalyst was prepared by an incipient wetness impregnation method using $H_2PtCl_6 \cdot 6H_2O$ (Kanto Chemicals) as the Pt precursor. An aqueous solution (11.4 mL) containing 1.03 g of $H_2PtCl_6 \cdot 6H_2O$ was added dropwise to 7.01 g of SiO_2. The impregnated sample was dried at 60 °C under reduced pressure and then calcined at 500 °C for 4 h in air. The resulting sample, denoted by 5 wt% Pt/SiO_2 (P), was stored in a dry box. The reduction of the 5 wt% Pt/SiO_2 (P) catalyst by H_2 was carried out before being used in the reaction.

Preparation of 5 wt% Ru/SiO_2 (P) Catalyst

The 5 wt% ruthenium on silica (CARiACT Q-6) catalyst was prepared by an incipient wetness impregnation method using $RuCl_3 \cdot 3H_2O$ (N.E. Chemcat) as the Ru precursor. An aqueous solution (6.3 mL) containing 0.54 g of $RuCl_3 \cdot 3H_2O$ was added dropwise to 4.00 g of SiO_2. The impregnated sample was dried at 60 °C under reduced pressure and then calcined at 500 °C for 4 h in air. The resulting sample, denoted by 5 wt% Ru/SiO_2 (P), was stored in a dry box. The reduction of the 5 wt% Ru/SiO_2 (P) catalyst by H_2 was carried out before being used in the reaction.

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