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Economical and efficient aqueous reductions of high melting-point imines and nitroarenes to amines: promotion effects of granular PTFE†

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The reductions of high melting-point imines and nitroarenes to amines in aqueous media using Zn powder, granular PTFE (polytetrafluoroethylene), catalytic Aliquat 336 and NH_4Cl or 5% NaOH at room temperature have been achieved. A major advantage of this procedure is that the cost of the catalyst is only 1/7200 of that of a previously reported nitroaromatic aqueous reduction catalyst. Altogether 13 imines and 11 nitroarenes were reduced to the corresponding amines with excellent yields. The effects of the amount of granular PTFE, and solubilities and melting points of the substrates, and melting points of the products on the reaction rates are discussed. For the first time, the relationship between the aqueous reaction rates and melting points of the products was investigated, which leads to a conclusion that lower melting-point products form faster than higher melting-point ones in the aqueous reductions. The Aliquat 336, granular PTFE and water are all recyclable.

Introduction

Amino functional groups are common in bioactive natural products and many pharmaceutically important substances.[1] Amines are usually obtained by the reduction of the corresponding imines.[2] Imines have been reduced by a wide variety of reagents including metal hydrides or metallic reagents, such as $NaBH_4$,[3] $NaBH_3(CN)$,[4] $NaBH(OAc)_3$,[5] $NaBH_4/Al_2O_3$,[6] $LiAlH_4$,[3a] $Zn(BH_4)_2/SiO_2$,[7] CaH_2/ZnX_2,[8] Bu_2SnClH,[9] $(\eta\text{-}C_5H_5)MoH_2$,[10] $RuHCl(PPh_3)_3$,[11] silane/MoO_2Cl_2,[2] $Ni(acac)_2/Et_2Zn$,[1a] $Pd(AcO)_2/Et_3SiH$,[12] In/NH_4Cl,[13] ZnB_2H_8,[14] and SmI_2.[15] In addition, metal-free hydrogen donors like $NH_3\text{–}BH_3$,[16] hydrogenation catalysts like Pd–C,[17] β-CD/$PdCl_2$,[18] Pt,[17] Co,[19] Ru,[20] and CF_3SO_3Zn,[21] and lanthanides such as Yb[22] have been used. All these reductions were performed in organic solvents. An aqueous enzymatic reduction has been reported for the synthesis of asymmetric amines[23] and an aqueous reduction using Zn powder has been used to produce amines in excellent yields.[24] However, in the aqueous systems only low melting-point substrates were investigated.

Another method leading to amines is the reduction of nitroarenes. A variety of procedures for these transformations have been reported. They include catalytic hydrogenations using Raney Ni,[25] Pd/C,[26] $PdCl_2$,[27] $Pd(OH)_2$,[28] $Pd/NaBH_4$,[29] Rh/C,[30] Ru/Al_2O_3,[31] Au/TiO_2,[32] Au/SiO_2,[32] PtO_2,[33] $Ag/NaBH_4$,[34] Pt/γ-Fe_2O_3,[35] or Co–Mo_2C/AC;[36] dissolving metal reductions using Fe/HCl,[37] or Sn/HCl;[38] and metallic reducing reagents using In,[39] Sm,[40] or $B_{10}H_{14}$.[41] In addition, $FeCl_3/N_2H_4$,[42] Se/NaOAc,[43] and TEOA/eosin Y[44] have been used to reduce nitro compounds to amines. Two elegant aqueous reductions have been reported by Tsukinoki[45] and Lipshutz,[46] but these require heating or expensive catalysts. In the other reduction systems, highly toxic, expensive, or moisture-sensitive reagents as well as organic solvents are necessary.

For the reduction of high melting-point imines and nitroarenes, it would be extremely beneficial to be able to replace the expensive catalysts and organic solvents with cheap reductants and green reaction media like water. As a solvent, water has a multitude of advantages including safety, nontoxicity, inflammability, cheapness, and environmental friendliness.

Results and discussion

When high melting-point imine (*E*)-*N*-(4-methoxybenzylidene)-1-naphthalenamine (**1h**) (2 g, mp: 100–102 °C, Table 1, entry 8) was subjected to the aqueous reduction conditions previously reported in the literature (Zn powder, 5% aq. NaOH solution at room temperature),[24] no reaction occurred after several hours and only a 50% conversion was achieved after 3 days. This indicates that the aqueous reductions of high melting-point imines are different from those of low melting-point imines. In an attempt to solve this problem, benzyltriethylammonium chloride was added to **1h** and the mixture was stirred under the

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† Electronic supplementary information (ESI) available: General experimental information, general procedure for the reduction of imines, control experiments for the function of Aliquat 336 and granular PTFE in the reduction of imines, control experiments for the function of PTC in the reduction of imines, general procedure for the reduction of nitroarenes, references, ^1H NMR and ^{13}C NMR spectra for new products. See DOI: 10.1039/c4ra04528a

‡ T. L., X. C., and L. S. contributed equally.

Table 1 Reduction of high melting-point imines to amines in water at room temperature[a]

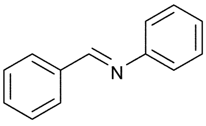
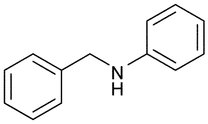
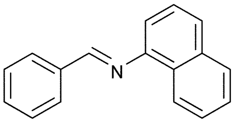
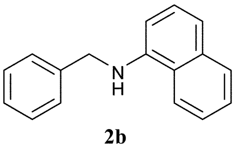
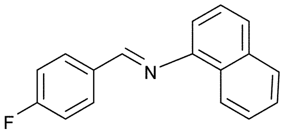
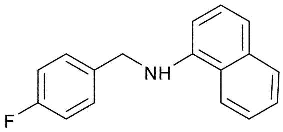
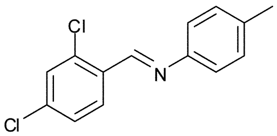
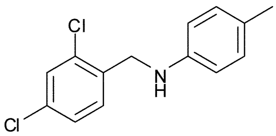
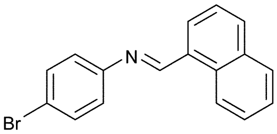
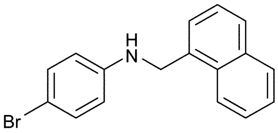
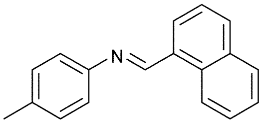
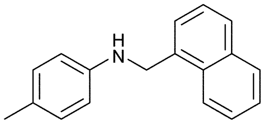
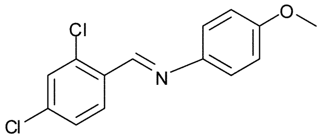
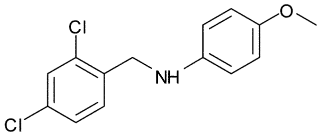
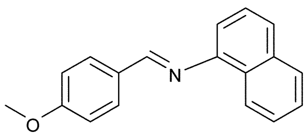
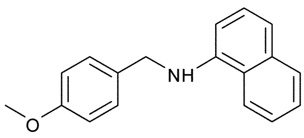
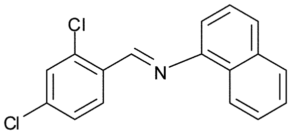
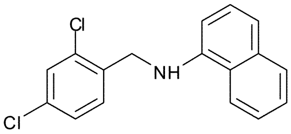
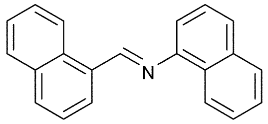
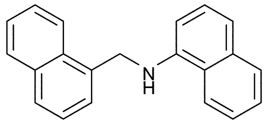
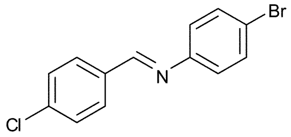
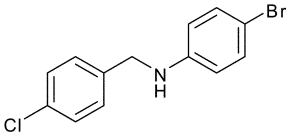
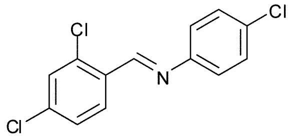
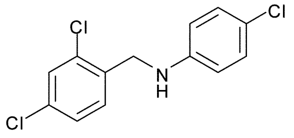
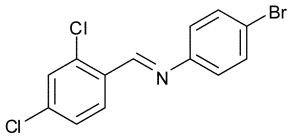
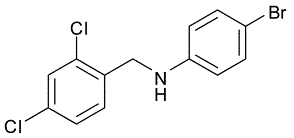
Entry	Imine	Solubility[b] (mol L^{-1})	Mp of imine (°C)	Reaction time (h)	Amine	Mp of amine (°C)	Yield[c] (%)
1	 **1a**	7.0×10^{-4}	51–52	0.67	 **2a**	Syrup at rt	85
2	 **1b**	3.4×10^{-5}	74–76	0.8	 **2b**	66–68	88
3	 **1c**	1.5×10^{-5}	85–86	1.5	 **2c**	Syrup at rt	89
4	 **1d**	9.4×10^{-6}	84–85	0.75	 **2d**	60–61	90
5	 **1e**	6.2×10^{-6}	85–86	1.5	 **2e**	88–90	86
6	 **1f**	1.3×10^{-5}	90–92	0.67	 **2f**	Syrup at rt	90
7	 **1g**	1.8×10^{-5}	99–101	0.8	 **2g**	Syrup at rt	89
8	 **1h**	3.7×10^{-5}	100–102	2.8	 **2h**	67–69	88
9	 **1i**	1.4×10^{-6}	111–113	1.3	 **2i**	Syrup at rt	93

Table 1 (*Contd.*)

Entry	Imine	Solubility[b] (mol L^{-1})	Mp of imine (°C)	Reaction time (h)	Amine	Mp of amine (°C)	Yield[c] (%)
10	 **1j**	4.3×10^{-7}	117–118	1.2	 **2j**	125–128	95
11	 **1k**	1.8×10^{-5}	128–129	1.8	 **2k**	78–79	89
12	 **1l**	4.0×10^{-6}	130–132	1.5	 **2l**	69–72	90
13	 **1m**	5.2×10^{-6}	134–137	0.75	 **2m**	Syrup at rt	92

[a] All conversions were 100%. [b] **1a–1i**, **1k–1m**: data from SciFinder; **1j**: data calculated using Software Wskow. [c] Isolated yields. Reaction conditions: imine (2 g), 5% aq. NaOH (10 mL), Aliquat 336 (0.06 equiv.), Zn powder (5 equiv.), and granular PTFE (5 g) at room temperature.

same conditions as above. After several hours, the reduction still did not take place. Other solid PTCs (phase transfer catalysts) such as tetraethylammonium chloride, and tetrabutylammonium bromide did not work either. When liquid PTC Aliquat 336 and 5 g of granular PTFE (PTFE sand, 70 pieces per g) were added to the reaction mixture with mechanical stirring,[47] the reduction was complete in 2.8 h and gave an yield of 88%.

Other imines (**1a–1m**, 2 g, mp: 70–140 °C) with low to high melting-points were suspended on a 5% aq. NaOH solution (10 mL) and treated with Aliquat 336 (0.06 equiv.), Zn powder (5 equiv.) and granular PTFE (5 g) at room temperature with mechanical stirring.[47] The corresponding amines were obtained in 0.6–3 h (Table 1, entries 1–13). The products of the reaction adhered to the granular PTFE. So when the reduction was complete, the aqueous solution was decanted and the residue was extracted with a small amount of ethyl acetate which was acidified with conc. HCl to give amine hydrochlorides **2a** (85%), **2b** (88%), **2c** (89%), **2d** (90%), **2e** (86%), **2f** (90%), **2g** (89%), **2i** (93%), and **2m** (92%). Alternatively the product was crystallized with ethanol after the ethyl acetate was evaporated to give **2h** (88%), **2j** (95%), **2k** (89%), and **2l** (90%). The reduction of **1d** was scaled up to 11 gram with similar yield (91%) in 8 h. The imines with lower melting points tended to react faster (**1a**, **1b**, **1d**, **1f**, **1g** *vs.* **1h–1l**) (Table 1, entries 1, 2, 4, 6, 7 *vs.* 8–12). The solubility of the imines was not an important factor in determining the reaction rates. This is different from our previous observation in the hydrolysis of steroidal epoxides.[48] One possible reason for this is that the differences in solubilities were not large enough and other factors dominated. However, the reaction rates of some of the reactions that produced liquid products (**2a**, **2f**, **2g**, **2m**) (Table 1, entries 1, 6, 7, 13) were faster than those that produced solid products (**2e**, **2h**, **2j**, **2k**, **2l**) (Table 1, entries 5, 8, 10–12). The reason is that the syrup products can serve as a solvent to dissolve the solid high melting-point imines, which accelerates the reduction. Halogen groups such as F, Cl, and Br remained intact after the reduction (Table 1, entries 3–5, 7, 9, 11–13).

The reduction of nitroarenes **3a–3k** using 7 equiv. of Zn powder, 2 equiv. of NH_4Cl, 0.06 equiv. of Aliquat 336, 5 g of granular PTFE and water with mechanical stirring[47] at room temperature are presented in Table 2. The conditions are applicable to both high and low melting-point nitroarenes. The reaction times ranged from 0.25 to 13 h and the yields were excellent. Nitroarenes with lower melting points tended to react faster (**3j** *vs.* **3k** *vs.* **3i**) (Table 2, entries 10 *vs.* 11 *vs.* 9). However, there were large differences in the reaction times for substrates with similar melting points (**3a** *vs.* **3b**) (Table 2, entries 1 *vs.* 2). The difference in the reaction rates between **3a** and **3b** is probably due to the lower solubility of **3b**. Although the solubilities of **3c** and **3d** (Table 2, entries 3 and 4) are higher than

Table 2 Reduction of nitroarenes to amines in water at room temperature[a]

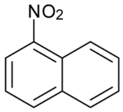
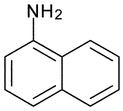
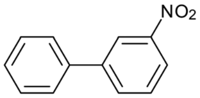
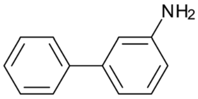
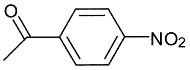
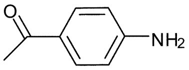
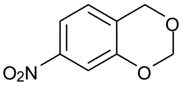
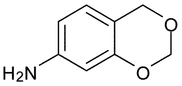
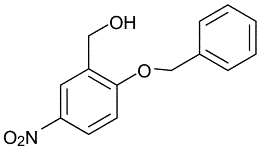
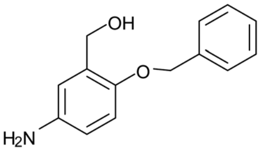
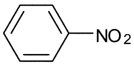
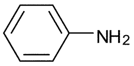
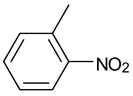
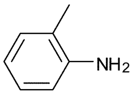
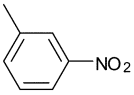
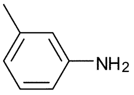
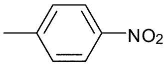
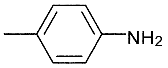
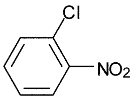
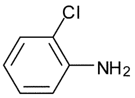
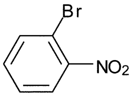
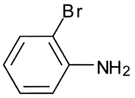
Entry	Nitroarene	Solubility[b] (mol L^{-1})	Mp of nitroarene (°C)	Reaction time (h)	Amine	Mp of amine (°C)	Yield[c] (%)
1	 **3a**	2.0×10^{-4}	60–61	0.5	 **4a**	48–50	87
2	 **3b**	2.7×10^{-5}	60–61	1.2	 **4b**	Syrup at rt	92
3	 **3c**	5.0×10^{-3}	80–81	13	 **4c**	100–102	86
4	 **3d**	4.1×10^{-3}	90–91	4.0	 **4d**	98–100	88
5	 **3e**	6.1×10^{-4}	96–97	1.4	 **4e**	112–114	90
6	 **3f**	1.5×10^{-2}	5–6	2.0	 **4f**	Syrup at rt	82
7	 **3g**	3.2×10^{-3}	−9–10	1.7	 **4g**	Syrup at rt	88
8	 **3h**	3.2×10^{-3}	15–16	2.7	 **4h**	Syrup at rt	86
9	 **3i**	3.2×10^{-3}	50–52	2.0	 **4i**	41–42	92
10	 **3j**	2.3×10^{-3}	30–32	0.25	 **4j**	Syrup at rt	91

Table 2 (*Contd.*)

Entry	Nitroarene	Solubility[b] (mol L^{-1})	Mp of nitroarene (°C)	Reaction time (h)	Amine	Mp of amine (°C)	Yield[c] (%)
11	 **3k**	1.9×10^{-3}	40–42	0.4	 **4k**	Syrup at rt	88

[a] All conversions were 100%. [b] **3a–3k**: data from SciFinder. [c] Isolated yields. Reaction conditions: nitroarene (2 g), Aliquat 336 (0.06 equiv.), NH_4Cl (2 equiv.), Zn powder (7 equiv.), granular PTFE (5 g), and water (20 mL) at room temperature.

those of **3a** and **3b** (Table 2, entries 1 and 2), longer reaction times for **3c** and **3d** than those for **3a**, **3b**, and **3f–3k** (Table 2, entries 1–2, 6–11) were required since the melting points of products **4c** and **4d** (Table 2, entries 3 and 4) are higher than those of products **4a**, **4b**, and **4f–4k** (Table 2, entries 1–2, 6–11). Obviously, lower melting-point products form faster than higher ones in the reductions. This is similar to what was observed in the imine reductions discussed above (Table 1). To our knowledge, this represents the first example that the effect of the melting points of products on the aqueous reaction rates has been investigated.[49] The procedure is chemoselective for nitro groups and carbonyl (**4c**), acetal (**4d**), benzyl ether (**4e**) and halogen (**4j**, **4k**) groups remained intact (Table 2, entries 3–5, 10–11).

The procedure for the reduction of nitroarenes previously reported in the literature requires heating to 80 °C with Zn powder, NH_4Cl and H_2O.[45] Under our reaction conditions, the reductions took place at room temperature. Recently, the Lipshutz's group reported a method for the reductions of nitroaromatics which uses Zn, NH_4Cl and catalytic TPGS-750-M in water at room temperature with excellent yields.[46] The comparison of reduction conditions between the two methods mentioned above and this work is listed in Table 3. Our reduction rates are generally higher than that reported by the Lipshutz's group but their yields are slightly higher than ours. Catalyst TPGS-750-M requires a two-step synthesis or is commercially available from Sigma-Aldrich.[46,50] A comparison of the cost between Aliquat 336 and TPGS-750-M is shown in Table 4. The per millimolar reaction cost of TPGS-750-M is 7200 times of that of Aliquat 336.

The effect of the amount of granular PTFE on the reaction rate was investigated and the results are presented in Table 5. When 100, 500 or 5000 mg of imine **1d** was stirred in the presence of 5 g of granular PTFE and 0.5, 2.5 or 25 mL of 5% aq. NaOH respectively at room temperature, the reactants were 100% converted in 0.83, 1.0, and 4.33 h respectively (Table 5, entries 1–3). With 1 g of granular PTFE, the corresponding times were 1.5, 1.66, and 11 h respectively (Table 5, entries 1–3). With no granular PTFE, the 100- and 500 mg scale reactions were complete in 11 and 12 h respectively (Table 5, entries 1–2) and the 5000 mg scale reaction was not complete even after 24 h (Table 5, entry 3). For the 5000 mg scale reaction, reducing the

Table 3 Comparison of two aqueous nitroarene reduction conditions with this work

Method	Zn (eq.)	NH_4Cl (eq.)	Catalyst	Granular PTFE	Stirring	Temp.	Time (h)	Yield (%)
Tsukinoki's[a]	7	2	None	None	Magnetic	80 °C	0.5–1	81–97
Lipshutz's[b]	5	1.2	TPGS-750-M	None	Magnetic	rt	0.5–8	88–99
This work	7	2	Aliquat 336	5 g/2 g of nitroarene	Mechanical	rt	0.25–13	82–92

[a] Ref. 45. [b] Ref. 46.

Table 4 Price comparison between Aliquat 336 and TPGS-750-M

Catalyst (CAS no.)	Price		
	Aldrich[a]	Xiamen Pioneer Technology Co., Ltd.[b]	Cost of 1 mmol reaction
Aliquat 336 (5137-55-3)	—	¥0.12 per g	¥0.003 per 0.024 g
2 wt % TPGS-750-M in H_2O (1309573-60-1)	¥10.8 per mL	—	¥21.6 per 2[c] mL

[a] http://www.sigmaaldrich.com/catalog/search?interface=All_ZH&term=733857&N=0&mode=match%20partialmax&focus=product&lang=zh&region=CN. [b] http://detail.1688.com/offer/1204581242.html. [c] Ref. 46.

Table 5 The effect of granular PTFE on the reaction rate of imine **1d** reduction

Entry	Amount of **1d**	Time, conversion[a] (granular PTFE, 5 g)	Time, conversion[a] (granular PTFE, 1 g)	Time, conversion[a] (granular PTFE, 0 g)
1	100 mg	0.83 h, 100%	1.5 h, 100%	11 h, 100%
2	500 mg	1.0 h, 100%	1.66 h, 100%	12 h, 100%
3	5000 mg	4.33 h, 100%	4.33 h, 75% 11 h, 100%	4.33 h, 58[b]%

[a] Determined by ^{1}H NMR. [b] The reaction was not complete after 24 h. Reaction conditions: **1d** (100 mg, 500 mg or 5000 mg), Zn powder (5 equiv.), 5% aq. NaOH (0.5 mL for the 100 mg scale reaction; 2.5 mL for the 500 mg scale reaction; 25 mL for the 5000 mg scale reaction), Aliquat 336 (0.06 equiv.), and granular PTFE at room temperature.

amount of granular PTFE from 1 to 0 g, resulted in a decrease in the yield at 4.33 h from 75% to 58% (Table 5, entry 3). These data indicate that the granular PTFE has a large promoting effect on the reaction rate.

Aliquat 336 probably serves as the reaction medium since it can dissolve the substrates; although it was only used in catalytic amount. Other PTCs such as benzyltriethylammonium chloride, tetraethylammonium chloride, tetrabutylammonium bromide, sodium dodecanesulfonate or liquid *N*-butyl-*N*-methyl imidazolium chloride are too hydrophilic and are not capable of dissolving imines and nitroarenes at room temperature (see ESI†). The granular PTFE functions as a co-stirrer to promote the efficiency of the stirring.[51] In the control experiments, the reduction did not occur when only Aliquat 336 was used as the solvent or in the absence of both Aliquat 336 and granular PTFE (see ESI†). Aliquat 336 may facilitate the electron transfer from the solid zinc to the imines (or nitroarenes) in this multiphasic system (solid Zn, solid substrate, solid granular PTFE, water, and liquid Aliquat 336).

In order to evaluate the reusability of the Aiquat 336, granular PTFE and water, the reduction of **1k** was investigated as a representative reaction (Table 6). After the first reduction cycle was complete, the reaction mixture was extracted three times in a flask with a minimal amount of toluene. The product was then crystallized with ethanol after toluene was evaporated. The concentrated mother liquor, fresh Zn powder and **1k** were then reintroduced to the flask. With each subsequent cycle, the amounts of zinc were gradually reduced from 5 to 3 equiv. and the reaction times were shortened from 2.83 to 1.08 h (Table 6). For all six cycles, the conversions were 100% and the reaction yields were excellent, indicating that the Aliquat 336, granular PTFE and water are highly recyclable in this reduction system.

Table 6 Recycling of Aliquat 336, granular PTFE and water in the reduction of imine **1k**[a]

Cycle No.	1	2	3	4	5	6
Zn (equiv.)	5	5	5	5	4	3
Time (h)	2.83	2	1.17	1.33	1.08	1.08
Yield[b] (%)	88	86	85	82	83	81

[a] All conversions were 100%. [b] Isolated yields. Reaction conditions: **1k** (200 mg), 5% aq. NaOH (10 mL), Aliquat 336 (0.06 equiv.), Zn powder, and granular PTFE (5 g) at room temperature.

Experimental

General experimental information

All of the chemicals were obtained from commercial sources or prepared according to standard methods. The ^{1}H NMR (400 or 600 MHz) and ^{13}C NMR (100 or 150 MHz) were recorded on a Bruker AM-400 spectrometer or a Bruker Avance III spectrometer respectively. Chemical shifts (δ) are reported relative to TMS (^{1}H) or $CDCl_3$ (^{13}C). IR spectra were recorded on BIO-RAD FTS 3000 spectrometer. Melting points were recorded on an X-4 Micro-melting Point Apparatus. High resolution mass spectra (ESI) were obtained on a Bruker micrOTOF-QII. All the aqueous reductions were performed in 100 mL flasks and agitated by a modified stirring rod. The stirring rod was modified by inserting a 25 cm PTFE wire into the blades and has been described previously.[47] The granular PTFE is 70 pieces per g.

General procedure for the reduction of imines

Zn powder (5 equiv.) was added to a mixture of imine (**1a–1m**, 2 g), Aliquat 336 (0.06 equiv.), granular PTFE (5 g) and 5% aq. NaOH solution (10 mL). The reaction mixture was mechanically stirred[47] for 0.6–2.8 h at room temperature. TLC (thin layer chromatography) was used to determine when the reaction was complete. The aqueous solution was decanted and the solid residue was extracted with a small amount of ethyl acetate followed by acidified with conc. HCl to give amine hydrochlorides: **2a** (85%), **2b** (88%), **2c** (89%), **2d** (90%), **2e** (86%), **2f** (90%), **2g** (89%), **2i** (93%), and **2m** (92%). This procedure was applied to the synthesis of **2d** (91%, 8 h) from 11 gram of **1d**. Alternatively the product was crystallized with ethanol after ethyl acetate was evaporated to give **2h** (88%), **2j** (95%), **2k** (89%), and **2l** (90%).

General procedure for the reduction of nitroarenes

Zn powder (7 equiv.) was added to a mixture of nitroarene (**3a–3k**, 2 g), Aliquat 336 (0.06 equiv.), NH_4Cl (2 equiv.), granular PTFE (5 g) and H_2O (20 mL). The reaction mixture was mechanically stirred[47] for 0.25–13 h at room temperature. TLC (thin layer chromatography) was used to determine when the reaction was complete. The aqueous solution was decanted and the solid residue was extracted with a small amount of ethyl acetate followed by acidified with conc. HCl to give amine hydrochlorides: **4a** (87%), **4b** (92%), and **4e** (90%). Alternatively after ethyl acetate was evaporated the product was crystallized with ethanol to give **4c** (86%), and **4d** (88%) or distillation under vacuum to give **4f** (82%), **4g** (88%), **4h** (86%), **4i** (92%), **4j** (91%), and **4k** (88%).

Conclusions

In conclusion, we have developed a new method using Aliquat 336, granular PTFE and Zn powder for the reduction of high melting-point imines and nitroarenes in aqueous media at room temperature. The relationships of the reaction rates with the amount of granular PTFE, the solubilities and melting points of the substrates and the products are discussed. The cost of our catalyst is much lower than those of the catalysts reported in the literature. The advantages of our procedure are fast, inexpensive, easy to carry out and in excellent yields. Since Aliquat 336, granular PTFE and water are highly recyclable, inexpensive, and safe, this procedure should be easily adaptable for industrial production.

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