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Sodium hydroxide-catalyzed transfer hydrogenation of carbonyl compounds and nitroarenes using ethanol or isopropanol as both solvent and hydrogen donor

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ABSTRACT

The development of a clean and renewable energy carrier has become a subject of high priority, and new catalytic system that involves both abundant and cheap catalysts and green solvents is highly desirable in terms of practical and sustainable chemistry. In this spirit, sodium hydroxide-catalyzed transfer hydrogenation of carbonyl compounds using ethanol as both hydrogen source and solvent is developed in this report. The process is successfully utilized in the hydrogenation of various ketones and aldehydes, and the corresponding primary and secondary alcohols are synthesized with excellent conversions. Furthermore, sodium hydroxide also smoothly promotes the transfer hydrogenation of nitroarenes providing anilines and azobenzenes. For both carbonyl compounds and nitroarenes, results in ethanol and isopropanol are compared, and a remarkable change of selectivity between these two solvents is disclosed for the NaOH-catalyzed transfer hydrogenation to nitroarenes.

1. Introduction

Economic, regulatory and environmental concerns have prompted a remarkably increasing demand for sustainable, practical and "green" catalytic processes [1]. This demand pushes industry and academia to shift their focus toward improvement of catalyst recovery, restriction of catalyst leaching, development of abundant, cheap and less toxic catalysts, as well as the use of green solvents [1a,2].

Reduction of carbonyl compounds yielding alcohols is a very important transformation in organic synthesis, its industrial application span, fine chemical conversions to pharmaceuticals synthesis. Direct hydrogenation with pressures of H_2 gas [3] and transfer hydrogenation from a hydrogen donor molecule [4] are two often employed strategies (Chart 1). As a key example of green catalysis, transfer hydrogenation methodology has become in recent years a center of attraction because it does not require pressurized hydrogen gas and elaborate experimental setups, the hydrogen donors are readily available, inexpensive, easy to handle, and the major side product (such as acetone) can be recycled.

Transition metal-catalyzed transfer hydrogenation of carbonyls, involving first-, second- and third-row transition metals of groups 8–10, has attracted growing interest owing to their high efficiency and selectivity [4,5]. However, the noble metals (such as Ru, Rh, Pd, Ir, Os and Pt) among them are very expensive, in addition, regulatory organizations limit the metal residual levels in pharmaceutical products to ppm or less levels because of their inherent toxicity. Although more abundant and biocompatible iron seems an excellent candidate for an economic and "greener" alternative, most of the reactions do not proceed in the absence of uneasy-to-get and environmentally-unfriendly ligands [6]. Furthermore, organocatalytic [7] and base-catalyzed transfer hydrogenation [8] have also emerged recently, and received considerable attention. The importance of the hydroxide bases [8] has been first illustrated in 2009 by the reports of the groups of Polshettiwar and Varma with KOH [8a] and Ouali et al., with NaOH [8b] without any transition metal complex for the hydrogenation of carbonyls by 2-propanol. In this context, we have further investigated base-catalyzed transfer hydrogenation.

In all cases of transfer hydrogenation, 2-propanol and formate are the mainly used "sacrificial" reducing sources and solvents. The use of a green solvent is one of the 12 principles of green chemistry [1a]. A green solvent must therefore, possess specific features including low toxicity, non-mutagenicity, widespread availability, and reproducibility. These common green solvents used in organic

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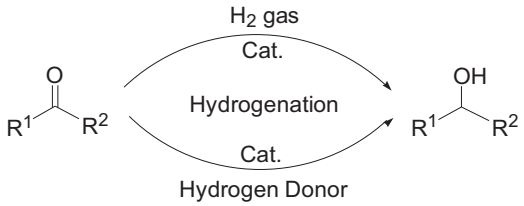


Chart 1. Hydrogenation of carbonyl compounds yielding alcohols.

synthesis include in particular H_2O, glycerine, EtOH, some ionic liquids, and supercritical CO_2. As one of renewable and cheapest reagents, ethanol, usually produced by fermenting starch, has the potential to be ideal an alternative to 2-propanol and formate in transfer hydrogenation [9]. However, the successful application of ethanol as hydrogen source was rarely reported [10], mainly due to its ability to produce stable transition metal complexes containing carbonyl with the catalysts that are used for the transfer hydrogenation process.

Nitro derivatives are a major family of polluants. Their reduction products of nitroarenes, functionalized anilines are important precursors and intermediates for the manufacture of pharmaceuticals, agrochemicals, pigments, dyes, rubbers, polymers, rubbers, corrosion inhibitors and photographic developers [11,12]. Reduction of poisonous nitroarenes [13] based on catalytic hydrogenation, metal mediated reductions and electrolytic reduction is the traditional synthesis methods for anilines [14]. Recently, catalytic transfer hydrogenation has emerged as a green and efficient route for the formation of anilines, however, the uses of expensive transition metals and/or ligands are necessary in the transformation [15], in addition, the product contamination by these noble metals restricts the application of such systems in several fields, and especially in biomedicine. Thus, it is highly desirable to develop more economic and pharmaceutically safe methodologies for synthesis of anilines, as well as degradation of nitroarenes.

Herein, we report that abundant and cheap NaOH promotes transfer hydrogenation of carbonyls including ketones and aldehydes compounds forming primary and secondary alcohols, respectively, using EtOH as both hydrogen source and solvent under relatively mild conditions. Additionally, nitroarenes are hydrogenated to form anilines and azobenzenes based on the NaOH-catalyzed transfer hydrogenation protocol with 2-PrOH as both hydrogen donor and solvent.

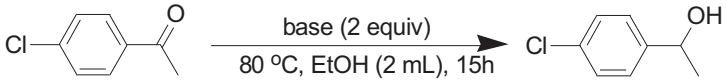
2. Results and discussion

2.1. Investigation of the optimal reaction conditions for transfer hydrogenation of carbonyl compounds

In a preliminary experiment, 4-chloroacetophenone **1a** was chosen as a test substrate to identify the optimal reaction conditions. The transfer hydrogenation was initially carried out using EtOH (2 mL) as hydrogen source and solvent, in the presence of 2 equiv of NaOH at 80 °C. The conversion increased with increased reaction time in the range of 1–15 h, providing 95% conversion (Fig. 1a). It was further found that the amount of NaOH is one of the most crucial factors for the formation. Within 15 h, fleetly decreased conversion was detected with the reduction of NaOH; 0.5 equiv of NaOH promoted transfer hydrogenation producing only 23% conversion (Fig. 1b). When 0.25 equiv of NaOH was used in the reaction, 78% conversion was obtained within 60 h, which revealed that NaOH played the role of catalyst in this transfer hydrogenation. Furthermore, the decreased conversion caused by the temperature reduction, was demonstrated (Fig. 1c). The secondary alcohol **2a** was obtained with conversions of 13%, 31%, and 52%, at temperatures of 50 °C, 60 °C, and 70 °C, respectively.

Then we examined the influence of different bases and hydrogen sources on the transfer hydrogenation of 4-chloroacetophenone **1a**. As shown in Table 1, the reaction did not proceed at all when K_2CO_3 and Na_2CO_3 were employed at 80 °C in EtOH (Table 1, entries 1 and 2). K_3PO_4 was able to promote the same reaction, albeit in poor conversion (9%) within 15 h. The transfer hydrogenation by EtOH also took place in the presence of other alkali hydroxides such as KOH and CsOH, the same cation effect being revealed: both KOH (33%) and CsOH (57%) being farther less active than NaOH (95%). The organic base Et_3N was not efficient at all for this transformation (entry 6). These results are in agreement with those reported by the groups of Ouali et al. [8] using 2-PrOH as solvent and hydrogen donor. The model reaction was further carried out in various alcoholic solvents (hydrogen sources), with NaOH as catalyst at 80 °C for 15 h. It was found that the reaction did not occur in H_2O nor in MeOH (entries 7 and 8). On the contrary, the transfer hydrogenation proceeded perfectly in EtOH or 2-PrOH, and the latter is more active than the former. From the point of view of the goal of an economic and environmentally friendly reaction solvent, renewable and cheap EtOH is clearly more favorable than 2-PrOH. In addition, the use of another primary alcohol, *n*-BuOH, produced the desired product **2a** with the conversion of 16%.

Table 1
Screening of bases and solvents (hydrogen sources) for the transfer hydrogenation of 4-chloroacetophenone promoted by NaOH.[a]



1a (1 mmol) **2a**

Entry	Base (2 equiv)	Solvent (1 mL)	Conversion (%)[b]
1	K_2CO_3	EtOH	0
2	Na_2CO_3	EtOH	0
3	K_3PO_4	EtOH	9
4	CsOH	EtOH	56
5	KOH	EtOH	33
6	Et_3N	EtOH	0
7	NaOH	H_2O	0
8	NaOH	MeOH	0
9	NaOH	EtOH	95
10	NaOH	*i*-PrOH	>99
11	NaOH	*n*-BuOH	16

[a] The reaction was carried out with 4-chloroacetophenone (1 mmol) in the presence of bases (2 mmol) in alcohols (2 mL) at 80 °C under a nitrogen atmosphere for 15 h.
[b] Conversion was determined by NMR.

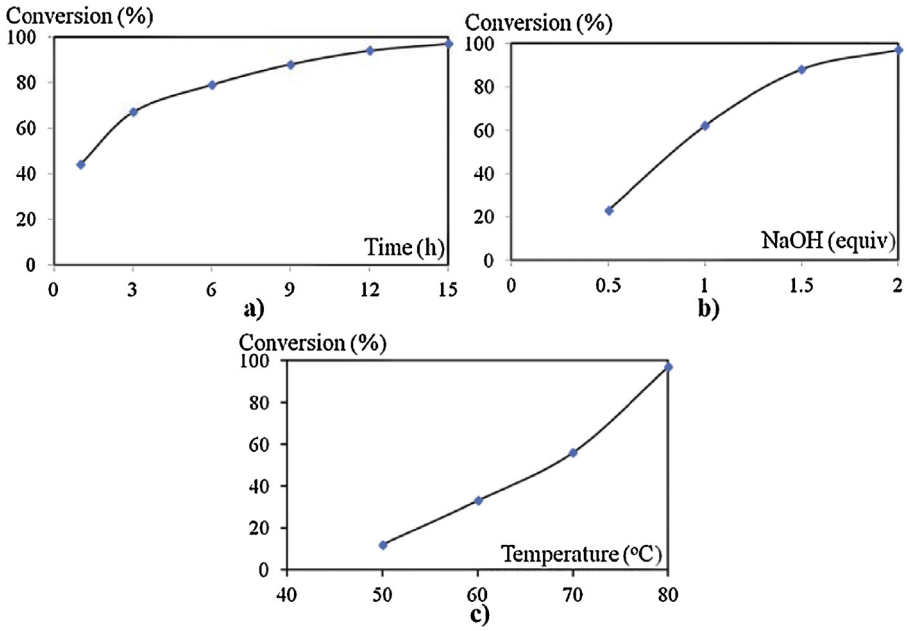


Fig. 1. (a) Reaction conditions: 4-chloroacetophenone (1 mmol), EtOH (2 mL), NaOH (2 equiv), 80 °C, *x* h; (b) reaction conditions: 4-chloroacetophenone (1 mmol), anhydrous EtOH (2 mL), NaOH (*x* equiv), 80 °C, 15 h; and (c) reaction conditions: 4-chloroacetophenone (1 mmol), anhydrous EtOH (2 mL), NaOH (2 equiv), *x* °C, 15 h.

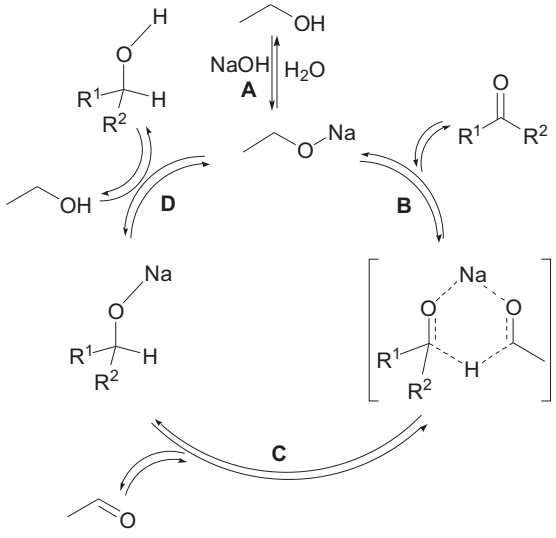
In summary, the transfer hydrogenation was performed smoothly with 95% conversion under the optimal reaction conditions involving 2 mL of EtOH, 15 h of reaction time, 2 equiv of NaOH, and 80 °C. This result, associated with the mild reaction conditions is even competitive with transition metal-catalyzed transfer hydrogenation; most importantly, this catalytic system is superior regarding the economic and environmental issue.

2.2. Investigation of the substrates scope for transfer hydrogenation of carbonyl compounds using EtOH as both solvent and hydrogen donor

Encouraged by the efficiency of the reaction protocol described above, the scope of the transfer hydrogenation was examined with 2 equiv of NaOH in EtOH under nitrogen atmosphere at 80 °C, and the results are gathered in Table 2. Acetophenone bearing electron-withdrawing (Cl and Br) as well as electron-donating (CH_3) groups in *para*-position were suitable substrates, and the desired secondary alcohols (**2a–c)** were efficiently produced with 92–95% conversions and 81–85% isolated yields (Table 2, entries 1–3). No direct correlation could be drawn between the outcome and the electronic nature of acetophenone substituents. When acetophenone without any substituent was employed, the corresponding product **2d** was obtained with 90% conversion and 76% yield (entry 4). The reaction with propiophenone was smoothly conducted under the optimized conditions, providing alcohol **2e** in 88% conversion. Moreover, the ketone containing two aromatic substituents was also investigated; benzophenone **1f** was successfully hydrogenated by EtOH with 94% conversion and 90% isolated yield. Interestingly, we successfully extended the transfer hydrogenation procedure to aromatic aldehydes **1g** and **1h**, and the corresponding primary alcohols **2g** and **2h** were synthesized in excellent conversions and yields. It was found that the presented protocol was also tolerant to aliphatic ketones, however, both conversion and yield were lower than those of aromatic ketones. Within 20 h, the transfer hydrogenation of cycloheptanone (**1i**) provided the corresponding product cycloheptanol (**2i**) with 66% conversion and 53% isolated yield (entry 9).

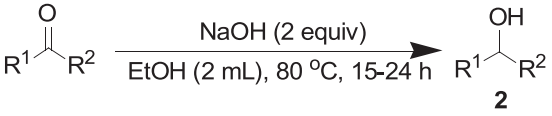
2.3. Proposed mechanism for naoh-promoted transfer hydrogenation of carbonyl derivatives using EtOH as hydrogen source

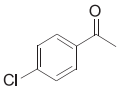
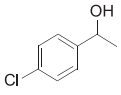
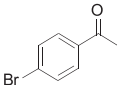
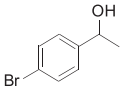
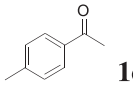
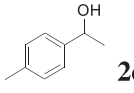
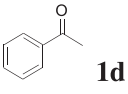
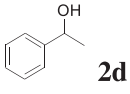
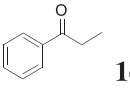
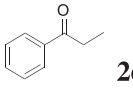
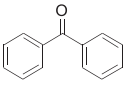
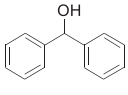
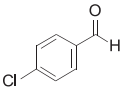
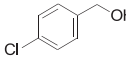
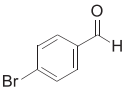
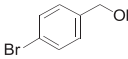
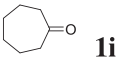
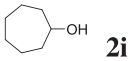
On the basis of Ouali et al.'s research of the mechanism on base-catalyzed transfer hydrogenation of carbonyls in 2-PrOH [8a], as well as the Meerwein–Ponndorf–Verley reduction mechanism [16a–d], the mechanistic proposal for the catalytic cycle involving EtOH as hydrogen donor and solvent is shown in Scheme 1. According to this mechanism, the catalytic cycle is drawn as an overall reversible process [16]. Firstly, ethanol reacts with sodium hydroxide forming sodium ethoxide that further produces a six-membered-ring intermediate through coordinating with carbonyl compounds. The decoordination step (step C) with hydrogen transfer proceeds to release acetaldehyde, and the key intermediate sodium alkoxide is produced. Alkoxide exchange



Scheme 1. Proposed mechanism for the NaOH-catalyzed transfer hydrogenation of carbonyl derivatives using EtOH as hydrogen source and solvent.

Table 2
Substrate scope of carbonyl derivatives for NaOH-catalyzed transfer hydrogenation using EtOH as hydrogen source and solvent.[a]



Entry	Substrates	Products	Time (h)	Conversion (%)[b,d]	Yield (%)[c,d]
1	 1a	 2a	15	95	83
2	 1b	 2b	15	93	85
3	 1c	 2c	24	92	81
4	 1d	 2d	18	90	76
5	 1e	 2e	24	88	80
6	 1f	 2f	24	94	90
7	 1g	 2g	18	89	82
8	 1h	 2h	18	88	83
9	 1i	 2i	20	66	53

[a] The reaction was carried out with carbonyls (1 mmol) in the presence of NaOH (2 mmol) in EtOH (2 mL) at 80 °C under nitrogen atmosphere.
[b] Conversion was determined by ^{1}H NMR.
[c] Isolated yields after column chromatography.
[d] ±2%.

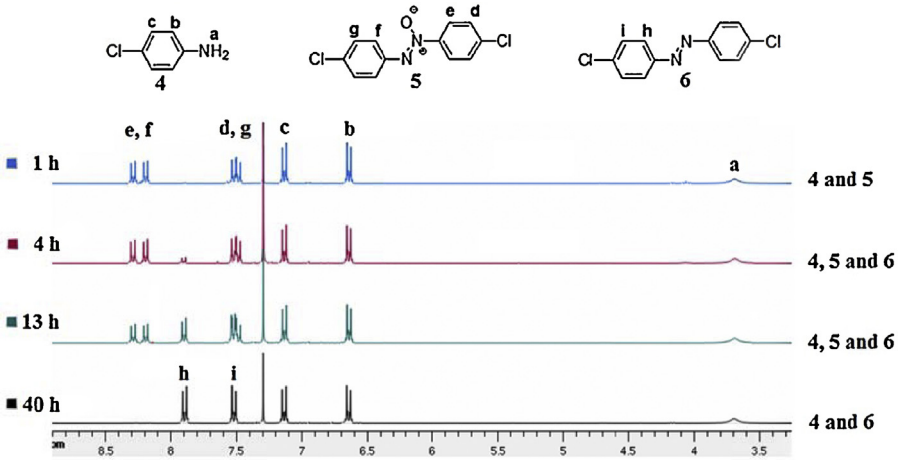


Fig. 2. ^{1}H NMR spectra of mixed products for transfer hydrogenation of 4-chloronitrobenzene. Reaction conditions: 1 mmol of substrate, 3 mL of 2-PrOH, 2 mmol of NaOH, 80 °C, under nitrogen.

of sodium alkoxide with another ethanol molecule leads to the formation of the desired alcohol and regeneration of sodium hydroxide.

2.4. NaOH-catalyzed transfer hydrogenation of nitroarenes

The transfer hydrogenation with 4-chloronitrobenzene was initially carried out in EtOH in the presence of 2 equiv of NaOH at 80 °C in the atmosphere of nitrogen for 6 h. It was found that 76% of the starting material **3** was converted into 4-chloroaniline **4**, azoxybenzene compound **5** and azobenzene compound **6** with 14%, 84% and 2% selectivities, respectively (Table 3, entry 1); the conversion of **3** was increased into 92% with 12% selectivity toward the desired 4-chloroaniline **4**, when the reaction time was prolonged to 10 h (entry 2). Interestingly, replacement of EtOH with 2-PrOH provided far better both conversion and selectivity toward **4**. The conversion of **3** and selectivity toward **4** was 100% and 63%, respectively, when the reaction proceeded in 2 mL of 2-PrOH within 1 h (entry 3). The volume of 2-PrOH slightly influences the percentage of **4** in the products mixture of **4** and **5**. The use of 3 mL of 2-PrOH gave higher selectivity toward **4** (67%) than that of both 2 and 6 mL of 2-PrOH (entries 3, 5 and 6). In addition, the result was not changed when 4 equiv of NaOH was employed (entry 4). Taking into account the interest of anilines, 2-PrOH was utilized as both hydrogen source and solvent in the subsequent study.

Subsequently, we observed that the transformation of the azoxybenzene **5** to the azobenzene **6** that is also an important precursor and intermediate in organic synthesis [11], started to proceed in 1 h in the presence of 2 equiv of NaOH using 3 mL of 2-PrOH as solvent (Figs. 2 and 3). The NMR analysis clearly revealed that the percentage (67%) of **4** in the mixture of reaction products did not obviously change in the range of 1–40 h (Fig. 3). The percentage of azobenzene compound **6** in the mixture of reaction product increased from 5% to 27% in the reaction time range of 4–24 h (Fig. 3, Table S1). The completed conversion of **5** into **6** was achieved in 40 h, and **6** was finally obtained with 33%, selectivity.

On the basis of previous studies [15a,e,17], the formulated catalytic mechanism is shown in Scheme 2. The preliminary step is the formation of sodium hydroxide through reaction of 2-PrOH with NaOH. Subsequently, both hydrogen transfer and Na^+ exchange between sodium hydroxide and 4-chloronitrobenzene proceed, giving acetone and intermediate **7**. Na^+ exchange of sodium in **7** with another 2-PrOH molecule then leads to the formation of key intermediate 4-chloronitrosobenzene **8** and the regeneration of sodium hydroxide. The *N*-phenylhydroxyamine **9** that is formed from **8** follows two distinct pathways A and B to generate **4**–**6**. Direct conversion to the aniline **4** is achieved via path A; path B proceeds to give the azoxybenzene **5**, which is converted to the azobenzene **6**. Further transfer hydrogenation of 6 to 4 does not proceed.

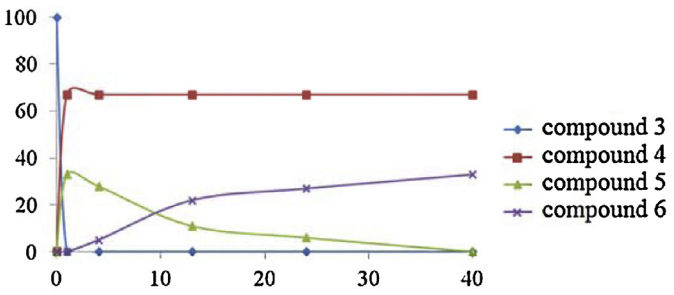
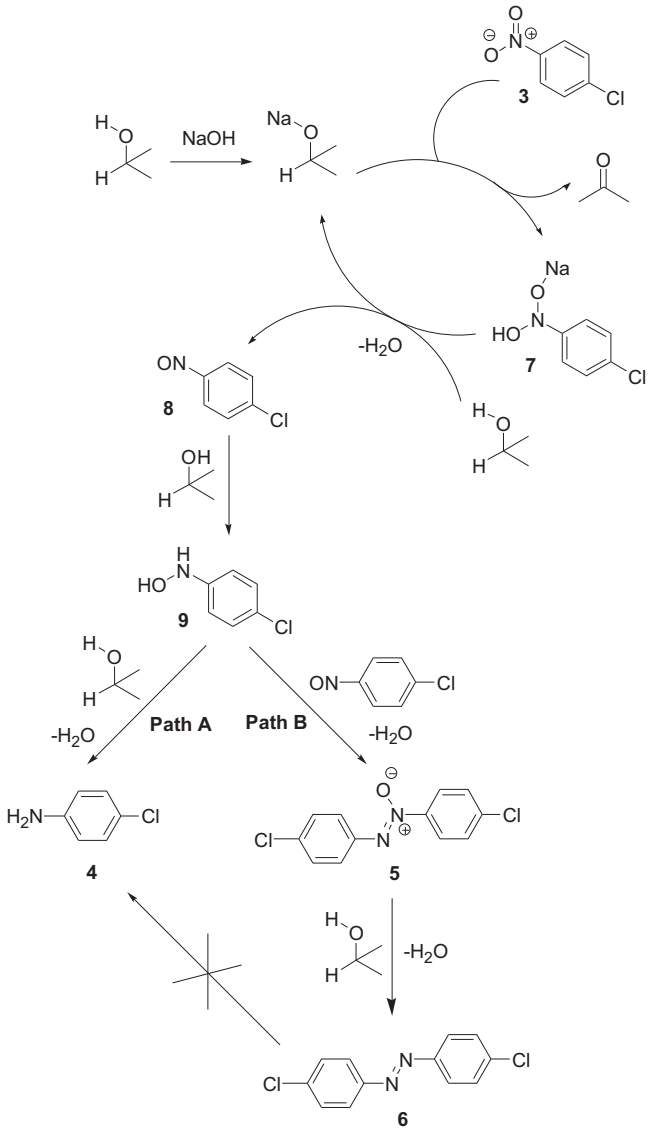


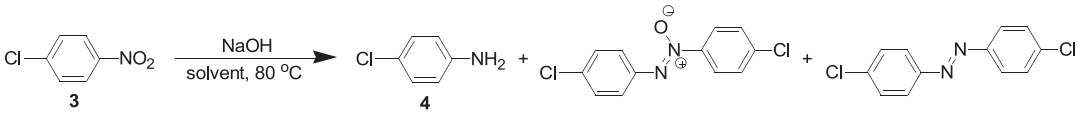
Fig. 3. Percentages of each compound upon increasing reaction time in the NaOH-promoted transfer hydrogenation of 4-chlorobenzene using 2-PrOH.



Scheme 2. Proposed mechanism for the NaOH-catalyzed transfer hydrogenation of 4-chloronitrobenzene using 2-PrOH as hydrogen source and solvent.

It was found that the transfer hydrogenation procedure with 4-chloronitrobenzene can be successfully extended to other nitroarenes (Table 4). In the case of nitrobenzene, the selectivity toward aniline is somewhat lower than that of 4-chloronitrobenzene, and the completion of transformation needed longer time (60 h). Transfer hydrogenation of 4-bromonitrobenzene and 3-iodonitrobenzene proceeded smoothly, providing 100% conversion from nitroarenes to anilines and azobenzenes (entries 3 and 4). When 4-fluoronitrobenzene was examined, the corresponding aniline and azobenzene were obtained within 60 h with only 37% and 22% conversions, respectively (entry 2). The reactions of nitrobenzenes containing electron-donating groups were then conducted with this protocol, as shown in Table 4; 4-methoxyl aniline was obtained with 54% conversion, and 4-methoxyl azobenzene was obtained with 46% conversion from the reduction of 4-methoxyl nitrobenzene (entry 5). The use of 2-methyl nitrobenzene gave much lower conversion even after prolonged reaction time, perhaps due to the influence of steric hindrance (entry 6).

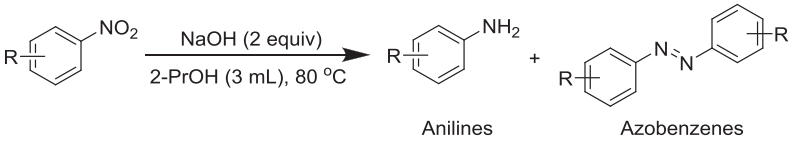
Table 3
Transfer hydrogenation of 4-chloronitrobenzene in the presence of NaOH using EtOH or 2-PrOH as both hydrogen source and solvent.

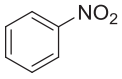
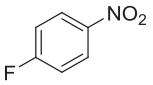
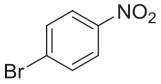
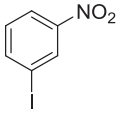
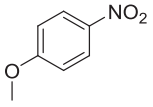
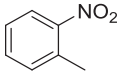


Entry	NaOH (equiv)	Solvent (mL)	Time (h)	Conversion of 3 (%)[a,c]	Selectivity (%)[b,c]		
					4	5	6
1	2	EtOH (2)	6	76	14	84	2
2	2	EtOH (2)	10	92	12	76	12
3	2	2-PrOH (2)	1	100	63	37	0
4	4	2-PrOH (2)	1	100	67	33	0
5	2	2-PrOH (3)	1	100	67	33	0
6	2	2-PrOH (6)	1	100	60	40	0

[a] Conversion was determined by ^{1}H NMR.
[b] Selectivity was determined by ^{1}H NMR.
[c] ±1%.

Table 4
NaOH-catalyzed transfer hydrogenation of nitroarenes forming the corresponding anilines and azobenzenes.



Entry	Nitroarene	Time (h)	Conversion (%)[a,b]	
			Aniline	Azobenzene
1		60	52	48
2		60	37	22
3		40	62	38
4		50	57	43
5		45	54	46
6		65	23	9

[a] The conversion was determined by ^{1}H NMR.
[b] ±2%.

3. Concluding remarks

In summary, we have shown that abundant, cheap sodium hydroxide was able to efficiently catalyze transfer hydrogenation of carbonyl compounds, without any transition metals and ligands, using the renewable and green solvent ethanol as both the hydrogen source and reaction solvent. In the process, ethanol is a highly interesting alternative to formic acid or 2-propanol as the hydrogen atom source. This catalytic system held several advantages, such as high efficiency, prevention of metal contamination of alcohol products (in particular pharmaceutically relevant products), simplicity of operation, economy, as well as sustainable and green nature. These results extend to ethanol; the findings by the groups of Polshettiwar and Varma with KOH [8a] and Ouali et al., with NaOH [8b] for the hydrogenation of carbonyls by 2-propanol. The mechanism proposed by the latter is privileged with this extension, and their results with 2-propanol that allows faster reactions than in ethanol as shown here are consistent with our data. These authors also adequately raised and carefully considered the possibility of catalysis of the reaction by sub-ppm traces of transition metal. However, the transition metals that are used to catalyze this reaction are reported to be efficient only in considerably higher quantities and with specific strongly activating ligands, so that this possibility cannot be retained.

Interestingly, it was observed for the first time that the degradation of poisonous nitroarenes into corresponding anilines and azobenzenes is readily achieved using the NaOH-catalyzed transfer hydrogenation protocol. This finding should be very helpful to solve the correlative problems of environmental pollution by nitroarenes and to provide an economic and green strategy for the synthesis of two common useful families of anilines and azobenzenes.

4. Experimental

4.1. General

All reactions and manipulations were performed under nitrogen using standard Schlenk techniques, unless otherwise noted. All commercially available reagents were used as received, unless indicated otherwise.

Flash column chromatography was performed using silica gel (300–400 mesh). ^{1}H NMR spectra were recorded with 300 MHz spectrometer, and ^{13}C NMR spectra were recorded at 75 with 300 MHz spectrometer.

4.2. Typical experimental procedure: transfer hydrogenation of carbonyl 1 using EtOH as solvent and hydrogen source in the presence of NaOH

A dried Schlenk tube (100 mL) equipped with a magnetic stirring bar was charged under a nitrogen atmosphere with **1** (130 μL, 1 mmol), NaOH (80 mg, 2 mmol), and EtOH (2 mL), then the Schlenk tube was sealed. The mixture was heated at 80 °C for 15–24 h. After cooling to room temperature, the solution was quenched with water (10 ml), the obtained mixture was then extracted with ethyl acetate (3 × 5 mL). The combined organic phase was washed with brine (2 × 5 mL) and dried over Na_2SO_4 and filtered. The filtrate was removed under reduced pressure to obtain the crude product that was further purified by silica gel chromatography (pentane/ethyl acetate as eluent) yielding pure **2**.

4.3. Typical experimental procedure: transfer hydrogenation of 4-chloronitrobenzene using 2-PrOH as solvent and hydrogen source in the presence of NaOH

A dried Schlenk tube (100 mL) equipped with a magnetic stirring bar was charged under a nitrogen atmosphere with 4-chloronitrobenzene **3** (1 mmol), NaOH (80 mg, 2 mmol), and 2-PrOH (3 mL), then the Schlenk tube was sealed. The mixture was heated at 80 °C for 40 h. After cooling to room temperature, 15 mL ethyl acetate was added into the mixture and filtered. The solvents were removed under reduced pressure to obtain the crude products that was analysed by ^{1}H NMR to determine the conversions.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata.2015.01.024.

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