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Fast and clean dechlorination of alkyl and aryl (poly)chlorides catalysed by bimetallic Ni–Al clusters in the presence of *t*-BuOH

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The dechlorination of alkyl and aryl (poly)chlorides is rapid and complete upon treatment with a new reduction system consisting of NaH as reagent, Ni–Al clusters as catalyst and *t*-BuOH as catalytic co-factor. The high efficiency of this combination is presumed to be due to the stabilization of the subnanometre nickel particles formed during reduction by the *in-situ*-generated alkoxide. Copyright © 2001 John Wiley & Sons, Ltd.

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INTRODUCTION

The reduction of organic halides, and especially of chlorinated arenes, is an important reaction, both for industrial and environmental concerns.[1] Several methods have been proposed for the destruction of these compounds, including transition-metal-catalysed hydrogenation[2] or reduction,[3] metal hydride reduction,[4,5] hydride or Grignard reagents[6,7] combined with transition metal salts or by activation of nickel(II) using an arene-catalysed lithiation process.[8] Among them, liquid-phase catalytic dehalogenation is of increasing interest because it is simple, effective at low temperature and excludes the formation of more toxic compounds such as dioxins. Very recently, we have discovered that nickel–aluminium clusters (de noted Ni–Al),[9] obtained by *tert*-butyl alkoxide (*t*-BuONa)-activated sodium hydride reduction of $Ni(OAc)_2$ and $Al(acac)_3$, is a new versatile catalyst for the reduction of alkyl and aryl (poly)halides under mild conditions (Scheme 1).[10]

$$\mathrm{R-X} \xrightarrow[\substack{\mathrm{NaH}/t\text{-}\mathrm{BuONa}\\ \mathrm{THF},\ 65^\circ\mathrm{C}}]{\mathrm{Ni-Al(10\,mol\%)}} \mathrm{R-H}$$

R = Alkyl or aryl
X = Cl or Br

Scheme 1.

The higher activity of bimetallic Ni–Al catalysts compared with those of monometallic nickel was attributed to the high dispersion of subnanometre nickel(0) particles in the aluminium oxide matrix obtained after *in situ* oxidation of the initially formed aluminium(0). We wish to report here that this Ni–Al catalyst, associated with an alcohol as co-factor and with sodium hydride (NaH) as reagent, produces a powerful and convenient reagent that allows fast and complete dechlorination of organic (poly)chloro derivatives. In the course of our earlier work on Ni–Al-mediated reductions, an increase of reaction rate was observed for hydroxyl-bearing chloroarenes. 4-Chlorophenol and pentachlorophenol were totally transformed in phenol, in respectively 0.25 h and 0.75 h whereas the simple chloroarene-like chlorobenzene required at least 0.75 h reaction time. The differences between the rates of reduction prompted us to examine the activity of NaH-containing Ni–Al clusters when dechlorinations were performed by addition of an alcohol, simultaneously with an alkyl or aryl

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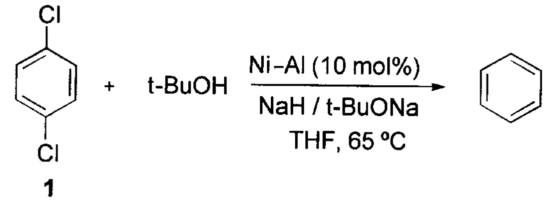


Scheme 2.

(poly)chloride, to the reduction catalyst. The results of this investigation are presented here.

RESULTS AND DISCUSSION

For our initial studies, we chose to examine the dechlorination of 1,4-dichlorobenzene **1** into benzene (Scheme 2). *t*-BuOH was selected as a representative alcohol since it cannot serve as a source of metal hydride by β-elimination. In order to examine the effect of the alcohol, various amounts of *t*-BuOH were added to the reaction media, simultaneously with 1,4-dichlorobenzene, and reaction times and conversions were determined. For all dechlorinations performed, the excess of NaH contained in the Ni–Al catalyst was systematically adjusted to the amount of *t*-BuOH added. The results are given in Table 1.

A control experiment indicates that **1** is quantitatively reduced in 1.5 h using our previously described Ni–Al clusters (Table 1, entry 1).[10] Interestingly, the rate of reduction was enhanced dramatically by the addition of *t*-BuOH. A rapid (less than 5 min) and complete dechlorination of 1,4-dichlorobenzene occurred using an excess (Table 1, entry 2), a stoichiometric (Table 1, entry 3) or catalytic amounts (0.5 or 0.2 equiv. per C—Cl unit) of *t*-BuOH (Table 1, Entries 4 and 5). Lowering the amount of alcohol to 0.15 or 0.1 equiv. resulted in increased reaction times. Nevertheless, complete dechlorinations were achieved within 15 min (Table 1, entries 6 and 7). These results indicate that a tertiary alcohol, like *t*-BuOH, is undoubtely a suitable activating agent for the Ni–Al-mediated dechlorination reaction. Moreover, results obtained using catalytic amounts of *t*-BuOH clearly demonstrate that this reduction did not proceed through hydrogenolysis of the carbon–chlorine bond over nickel(0) clusters by molecular hydrogen produced by the reaction of the alcohol with NaH. This suggests that the actual catalyst in the reaction is formed only when an appropriate amount of alcohol is present and that the active species are not solely nickel(0) or nickel hydride, which are thought to be formed in classical nickel-catalysed reductions.[8] Therefore, colloidal suspensions of the Ni–Al catalysts were observed before and after reduction by transmission electron microscopy (TEM). The TEM micrographs revealed that a significant fragmentation of nickel particles occurred during dechlorinations performed in the presence of *t*-BuOH. For example, after reduction of 1,4-dichlorobenzene in the presence of *t*-BuOH, the TEM micrographs revealed the presence of subnanometre (<0.5 nm) clusters, whereas the initial bimetallic Ni–Al catalyst was found to be constituted of nickel particles of around 1.5 nm. This result seems to indicate that the activating effect of the alcohol added with 1,4-dichlorobenzene is directly related to the bulk of the metallic particles. The higher performance of these catalysts compared with those used without alcohol might, therefore, be due to the increased stabilization of subnanometre metallic particles by the *in-situ*-generated alkoxide. Moreover, the use of the Ni–Al catalyst in combination with other ligating compounds like alkoxides (NaOEt, NaO-*i*-Pr) or anions of methylene bis-activated substrates ($NaCH(CO_2Et)_2$, NaAcac), generated *in situ* by reaction with NaH, is equally effective in these reductions, and the corresponding hydrocarbons were obtained in almost comparable yields. Finally, it is noteworthy that such fast and complete dechlorinations could only be observed with bimetallic Ni–Al catalysts. Reduction of 1,4-

Table 1 Influence of the amount of t-BuOH on the Ni–Al-catalysed reduction of 1,4-dichlorobenzene[a] (Scheme 2)

Entry	*t*-BuOH equivalent per C—Cl unit	NaH content (mmol)	Conversion (%)[b]	Reaction time (min)[b]
1	–	116	100	90
2	2	196	100	<5
3	1	156	100	<5
4	0.5	136	100	<5
5	0.2	124	100	<5
6	0.15	122	100	15
7	0.1	118	100	15

[a] Reactions were performed on 20 mmol of 1,4-dichlorobenzene using 4 mmol $Ni(OAc)_2$ and 4 mmol $Al(acac)_3$ for catalyst preparation.
[b] Determined by GC analysis.

dichlorobenzene using 10 mol% of the previously described monometallic nickel catalyst[11] in combination with *t*-BuOH afforded only 59% benzene, along with chlorobenzene (27%) and unreacted starting material (11%), after 10 h reaction time.

Having optimized the reaction conditions for complete 1,4-dichlorobenzene dechlorination, a series of further trials was undertaken with representative organic halides to corroborate the efficiency of the process. As can be seen in Table 2, the Ni–Al/*t*-BuOH system is effective for primary, secondary, tertiary and aryl (poly)chlorides. Note that: (i) no elimination products were detected for primary (Table 2, entry 1) and secondary (Table 2, entry 2) aliphatic halides; (ii) 1-chloroadamantane (Table 2, entry 3) is rapidly and quantitatively transformed into adamantane. In the aromatic series, chlorobenzene (Table 2, entry 4) and 1-chloronaphthalene (Table 2, entry 5) are readily reduced and the presence of electron-donating or electron-withdrawing substituents on the benzene ring had no effect (compare entries 4, 6, 7 and 8 in Table). Ketonic carbonyl groups are tolerated. 4-Chlorobenzophenone gave 81% of the expected reduced product, benzophenone, accompanied by 15% diphenylmethanol resulting from over-reduction (Table 2, entry 8). However nitrile or aldehyde functions are simultaneously reduced with the carbon–chlorine moiety in refluxing tetrahydrofuran (THF). Further experiments confirmed that dechlorinations of aryl di- and tri-chlorides exhibited similar trends to those observed with the simple aryl chloride. The result obtained with 4,4′-dichlorophenyl, a representative substrate of polychlorobiphenyls, is particularly significant for the efficiency of our reagent (Table 2, entry 11). Treatment of this compound with Ni–Al/*t*-BuOH at 65 °C in THF gave 100% dechlorination in less than 5 min, and only biphenyl was recovered. Finally, the dechlorination of the well-known 1,2,4,5-tetrachlorobenzene (Table 2, entry 13) was improved appreciably compared with our previous results.[10] The complete reduction was achieved in 150 min with the *t*-BuOH-modified Ni–Al catalyst, whereas 8 h were necessary with our classical catalyst. Note that the latter gave only 1,2,4-trichlorobenzene after 2 h reaction time.

In summary, we demonstrate the novelty and the efficiency of the NaH-containing Ni–Al clusters associated with *t*-BuOH in dechlorination reactions. Convenience, mildness and rapidity of the reaction associated with high yields and with the use of readily available reagents make the present method very attractive for the reduction of a wide range organic halides, and especially of aryl (poly)chlorides.

EXPERIMENTAL

Materials and instrumentation

THF was distilled from benzophenone–sodium adduct and stored over sodium wire. *t*-BuOH (Aldrich) was distilled from sodium. NaH (65% in mineral oil, Fluka) was used after three washings with 20 ml of THF under a nitrogen atmosphere. Nickel acetate [$Ni(CH_3COO)_2$] (Fluka) was dried under vacuum (20 mmHg) at 110 °C for 12 h. The water content after drying was lower than 0.5 mol%. Aluminium acetylacetonate [$Al(CH_2COCH_2COCH_3)_3$] (97%, Acros) was used without further purification. The progress of reactions was monitored using a Shimadzu GC-17 capillary gas chromatograph fitted with an "Optima 5" column (22 m × 0.25 mm, ID × 0.25 μm). All quantifications of reaction constituents were achieved by gas chromatography (GC) using a known quantity of decane as reference standard.

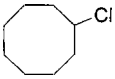
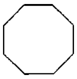
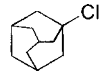
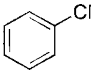
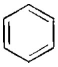
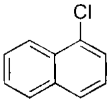
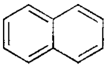
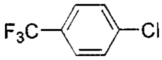
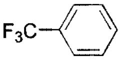
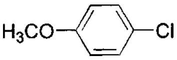
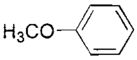
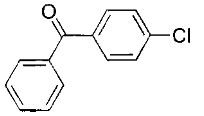
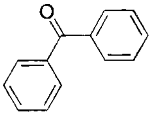
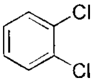
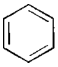
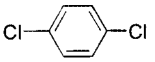
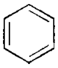
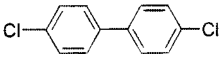
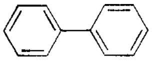
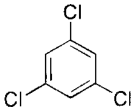
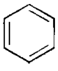
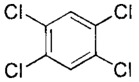
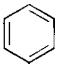
Characterization of Ni–Al nanoparticles

Characterization of Ni–Al clusters was performed using TEM. The TEM specimens were prepared by placing a drop of colloidal solution onto a carbon film supported on a copper grid and were studied using a Philips CM20 with LaB_6 cathode operating at 200 kV. Energy-dispersive X-ray spectra were recorded by means of an EDAX spectrometer equipped with an ultrathin window and an Si–Li detector. The analysis was carried out in nanoprobe mode with a probe diameter of 10 nm. The presence of the Al Kα peak at 1.486 keV and the Ni Kα peak at 7.47 keV was observed.

Representative procedure

Reduction of 1,4-dichlorobenzene: to a suspension of degreased NaH (124 mmol) in THF (20 ml) was added $Al(acac)_3$ (4 mmol) and $Ni(OAc)_2$ (4 mmol) and the mixture was heated at 65 °C under a nitrogen atmosphere. A solution of *t*-BuOH (8 mmol) in THF (5 ml) was then added dropwise and the mixture was further stirred under reflux for 5 h. A solution of 1,4-dichlorobenzene (20 mmol) and *t*-BuOH (8 mmol) in THF (10 ml) was then added to the dark-grey suspension of the Ni–Al clusters and the products were detected by GC analysis. At the end of the reduction, 10 ml of water

Table 2 Reduction of organic chlorides using Ni–Al catalyst and t-BuOH[a]

Entry	Substrate	Product	Reaction time (min)[b]	Conversion (%)[b]	Yield (%)[b]
1	$CH_3(CH_2)_9Cl$	$CH_3(CH_2)_8CH_3$	<5	100	Quant.
2			<5	100	Quant.
3			<5	100	Quant.
4			<5	100	Quant.
5			<5	100	96[c]
6			<5	100	Quant.
7			<5	100	Quant.
8			<5	100	81[c],[d]
9			<5	100	Quant.
10			<5	100	Quant.
11			<5	100	89[c]
12			<5	100	Quant.
13			150	100	Quant.

[a] Reactions were performed on 20 mmol organic chloride using a catalyst loading of 10 mol% per C—Cl unit. Reaction conditions for the reduction of alkyl and aryl monochlorides: 62 mmol NaH, 2 × 4 mmol *t*-BuOH, 2 mmol $Ni(OAc)_2$ and 2 mmol $Al(acac)_3$. Reaction conditions for the reduction of aryl dichlorides: 124 mmol NaH, 2 × 8 mmol *t*-BuOH, 4 mmol $Ni(OAc)_2$ and 4 mmol $Al(acac)_3$. Reaction conditions for the reduction of 1,3,5-trichlorobenzene: 186 mmol NaH, 2 × 12 mmol *t*-BuOH, 6 mmol $Ni(OAc)_2$ and 6 mmol $Al(acac)_3$. Reaction conditions for the reduction of 1,2,4,5-trtrachlorobenzene: 248 mmol NaH, 2 × 16 mmol *t*-BuOH, 8 mmol $Ni(OAc)_2$ and 8 mmol $Al(acac)_3$.

[b] Unless otherwise noted, determined by GC.

[c] Isolated yield by flash chromatography.

[d] Isolated with 15% diphenylmethanol.

was added dropwise at 0 °C (note that the low amount of residual hydride ensured a safe hydrolysis step for complete reactions). Except for benzene, the products obtained were characterized by ^{1}H and ^{13}C NMR spectroscopic comparisons with authentic samples.

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