Iron nanoparticle-promoted Cu (I)-catalysed homocoupling of arylmethyl halides for the synthesis of 1,2-diarylethanes

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Carbon–carbon bond formation is important in organic synthesis for the preparation of natural products, organic materials and polymers and so on. An efficient and mild reductive homocoupling of arylmethyl halides is now described. Treatment of various benzylic halides in the presence of zero valent iron nanoparticles (nZVI) and a catalytic amount of CuBr in air and water at room temperature afforded 1,2-diarylethanes in excellent yields.

Keywords: iron nanoparticles, benzylic halides, reductive homocoupling, C–C bond formation, Cu (I) catalysis, 1,2-diarylethanes, reaction in water

The development of useful reagents and efficient catalysts which enable carbon–carbon bond formation is key to contemporary organic synthesis. Reductive metal-catalysed homocoupling and cross-coupling reactions have played crucial roles in these bond formations over recent decades. These coupling reactions have been widely employed for the preparation of natural products, building blocks for supramolecular chemistry and self-assembly, organic materials and polymers, and lead compounds in medicinal chemistry from simpler entities.[1,2]

The reductive coupling of organic halides is an important method for C–C bond formation, where Wurtz[3] and Ullmann[4] reactions are classical methods for the preparation of bialkyl and biaryl compounds. Transition metal catalysed coupling reactions between organic electrophiles and organometallic compounds constitute the most straightforward approach for the formation of C–C bonds.[5] Several metals and metal complexes, such as titanium,[6] vanadium,[7] chromium,[8] lanthanum,[9] copper,[10] nickel,[11] zinc[12] and iron,[13] have been employed in this type of reaction.

The homocoupling of several organic halides has been performed in good yields under inert gas atmosphere and anhydrous conditions, in some cases using activated metals,[14] and the interest for these reactions has increased.[15] Advances in metal-promoted Barbier-type additions to carbonyl compounds in aqueous media[16] led to the hope that a Wurtz-type coupling could also be performed in water.

Water is a desirable solvent because it is safe, non-toxic, environmentally friendly, readily available and cheap compared to organic solvents.[17] Since the pioneering studies on Diels–Alder reactions by Breslow,[18] there has been increasing recognition that organic reactions can proceed well in aqueous media and offer advantages over those occurring in organic solvents.[17]

In 2007, Liu *et al.* reported that reductive homocoupling of benzylic halides with metallic iron powder in the presence of a catalytic amount of a cuprous salt in aqueous media leading to the corresponding bibenzyls. CuBr was the most efficient cuprous halide that they used in this type of reaction.[19] However, their procedure has drawbacks such as long reaction times (1–2 h), in some cases, fairly low yields of the products (down to 48%) and relatively high reaction temperatures (up to 90 °C).

Recently transition-metal nanoparticles have attracted attention; their preparation, structure determination, and applications are of interest.[20] One of these applications is their use in reactions generating C–C bonds.[21]

We now report the use of zero valent iron nanoparticles (nZVI) with water as the solvent in air in the presence of CuCl under mild reaction conditions.

Experimental

All reagents and solvents were purchased from Merck Chemical Company and used without further purification. All yields refer to products isolated by column chromatography or crystallisation. IR spectra were run on a Perkin-Elmer 781 spectrophotometer. NMR spectra were recorded on a Bruker Avance DPX-250. The purity of both starting materials as well as the reaction products were checked by TLC on silica-gel polygram SILG/UV254 plates or by a Shimadzu Gas Chromatograph GC-10A instrument with a flame-ionisation detector using a 15% carbowax 20M chromosorb-w acid washed 60–80 mesh column. TEM images of nanoparticles were obtained using a Philips model TM 200 FGE electron microscope.

Synthesis of nZVI

Iron nanoparticle was synthesised according to the reported method.[22] A water solution of 5×10^{-2} M of sodium luryl sulfate (SDS) was added into a clear solution of ferric chloride (0.026 mol) dissolved in 72 mL of ethanol and 21.6 mL of deionised water. Then a solution of potassium borohydride (0.08 mol) dissolved in 42 mL of ethanol and 10 mL of deionised water was added gradually and mixed with the above solution under constant and vigorous stirring. Stirring was continued for a further hour after a black precipitate was first formed. Then the products were separated and rinsed with ethanol and acetone, respectively. Reactions were run under nitrogen atmosphere. The average particle size and surface area were about 12 nm and 70 $m^2\ g^{-1}$ respectively (Fig. 1).

Preparation of 1,2-Diphenylethane (**2a**)

A suspension of iron nanoparticles (0.205 g, 2.2 mol) and CuBr (0.029 g, 0.2 mmol) in H_2O (5 mL) was stirred at room temperature for 10 min. Then benzyl brimide (0.342 g, 2 mmol) was added to the reaction mixture which was stirred for a further 25 min. Next, the solid was filtered off and washed with hot water (2 × 10 mL). The water solution stood at 5 °C for 2 h. Then the crude solid product (0.178 g, 98%) was isolated by filtration and recrystallised from methanol to give pure 1,2-diphenylethane **2a** (Table 1).

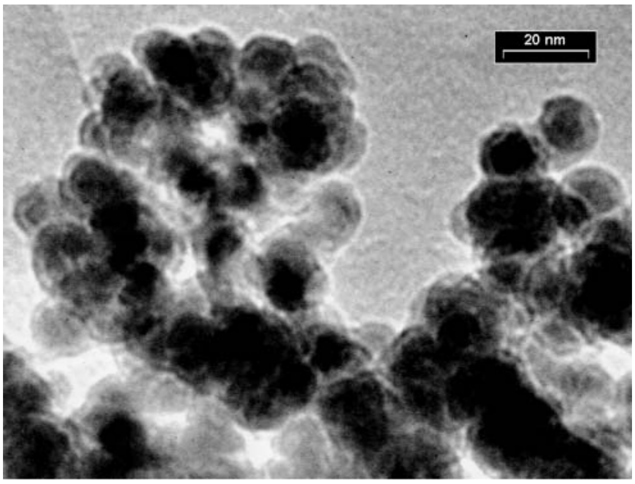

Fig. 1 TEM images of zero valent iron nanoparticles (average particle size = 12 nm).[22]

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Results and discussion

As part of our current studies on the development of efficient and simple methods for the preparation of organic compounds from readily available building blocks, we report here an improvement of homocoupling of benzylic halides under mild conditions. Thus a mixture of an arylmethyl halide **1**, iron nanoparticles[22] and a catalytic amount of CuBr in air and water undergoes a reductive homocoupling reaction at room temperature to afford 1,2-diarylethanes **2** in 88–98% yields (Scheme 1, Table 1).

All the reactions went to completion within 25 min. ^1H NMR analysis of the reaction mixtures clearly indicated the formation of the corresponding 1,2-diarylethanes **2** in excellent yields.

A range of 1,2-diarylethanes **2** were synthesised by reductive homocoupling reactions of the corresponding arylmethyl halides. The results are given in Table 1. The structures of the isolated 1,2-diarylethanes were confirmed by comparison of their spectral data (^1H NMR spectra) and their melting points with those of authentic samples (see Table 1).

A mechanistic rationalisation for this reaction is provided in Scheme 2. On the basis of the chemistry of metal-catalysed coupling reactions,[23] it is reasonable to assume that Cu(0) could be the active catalytic species, which is generated in the presence of iron nanoparticles by reduction of Cu(I). This active catalytic species could undergo two successive oxidative addition of the halide **1** to form intermediate **4** via **3**. Reductive elimination of 1,2-diarylethane **2** may form Cu(I) species which would complete the catalytic cycle.

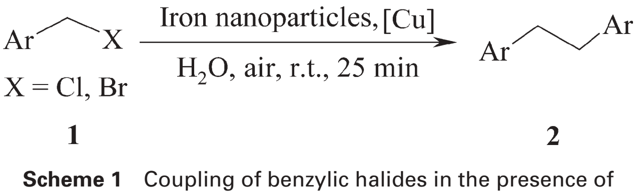
Conclusion

In conclusion, we have developed an efficient and mild Cu (I) catalysed reductive homocoupling of arylmethyl halides promoted by zero valent iron nanoparticles leading to 1,2-diarylethanes. Use of water as a green medium, carrying out the reactions in air without any need to inert gas atmosphere, fairly fast reaction times, reduced reaction temperature, excellent yields of the products and a simple purification process are the main advantages of this method.

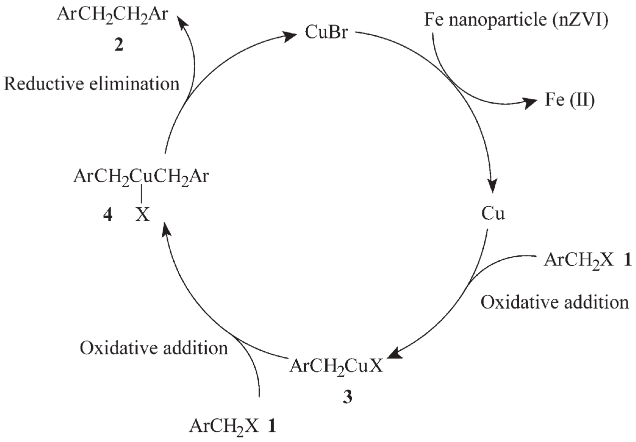
Table 1 Coupling of various arylmethyl halides with iron nanoparticles catalysed by CuBr in water

Entry	Ar	X	M.p./°C (lit)	Yield of 2/%[a]
a	C_6H_5	Br	50–51 (51–52)[24]	98
b	C_6H_5	Cl		92
c	4-ClC_6H_4	Br	98 (98–99)[25]	97
d	4-ClC_6H_4	Cl		87
e	4-NCC_6H_4	Br	198–199 (200–201)[26]	93
f	4-NCC_6H_4	Cl		88
g	4-$O_2NC_6H_4$	Br	182–184 (183–184)[27]	90
h	4-$O_2NC_6H_4$	Cl		88
i	4-$H_3CC_6H_4$	Cl	80–81 (82)[26]	90
j	4-$CH_3OC_6H_4$	Cl	124–126 (125.5–126.5)[28]	96
k	3-Br-4-$CH_3OC_6H_3$	Cl	145–147 (146.5–147.5)[28]	94
l	3-$F_3CC_6H_4$	Cl	76 (77–78)[29]	90
m	4-BrC_6H_4	Cl	113–114 (114)[30]	91
n	9-fluorenyl	Cl	241–242 (243–243.5)[29]	87
o	1-naphthyl	Cl	160–162 (161–162)[31]	88
p	2-naphthyl	Cl	186 (185–186)[32]	93
q	3-NCC_6H_4	Br	159–160 (159–161)[33]	92

[a] Isolated yield.



Scheme 1 Coupling of benzylic halides in the presence of nZVI and cuprous salt.



Scheme 2 Proposed reaction mechanism of coupling of benzylic halides in the presence of nZVI and CuBr.

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