Sonoelectroreduction of Metallic Salts: A New Method for the Production of Reactive Metallic Powders for Organometallic Reactions and Its Application in Organozinc Chemistry

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The reactivity of ultrafine zinc powders, produced by a new electrochemical method coupled to the use of ultrasound, has been evaluated for various organometallic reactions such as the Reformatsky reaction, Barbier allylation, alkyne reduction, reductive dehalogenation and *p*-nitroester cleavage. The results show that zinc powders produced by sonoelectrochemistry are highly reactive. Particle-size effects, reactivity of zinc-copper alloys and metal-waste recycling procedures have also been studied. The production of highly reactive zinc powder by sonoelectrochemical methods appears to be an interesting alternative to conventional methods used in organozinc chemistry and may be especially important in medium- or large-scale processes.

Introduction

The formation of organometallic compounds by the reaction of organic substrates with finely divided metal powders is a powerful tool for the synthetic chemist. Direct reaction with zero-valent metal is the only viable synthetic method for the production of most of these compounds because, for a large number of functional groups (e.g. ketone, ester, aldehyde, nitrile, epoxide), preparation by transmetallation starting from organomagnesium or organolithium reagents is not possible. However, the low reactivity of the majority of commercial zero-valent metals requires physical or chemical activation through a nonclassical preparation method.[1–5] Adsorption of the freshly prepared zero-valent metal on graphite[4] or titanium oxide[6] are excellent activation methods although this implies the initial chemical reduction of metal salts to prepare the zero-valent metal. Of the numerous metals used in organometallic chemistry, zinc plays a particularly important role due to its low cost with respect to many other metals, its versatility and also to the fact that it can be used with water as solvent.[8–14]

The present paper describes a new method for the preparation of highly active, finely divided zinc metal. The advantages of this new method are its low cost, the use of water as a solvent, its versatility and, most important, the possibility it offers for recycling the zinc salt obtained at the end of the reduction step of the organic substrate. In organozinc chemistry, the zinc salt obtained at the end of the reaction is always considered to be a by-product which is removed from the reaction and then either discarded or, in industry, stockpiled and eventually recycled for other uses.

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Metallic zinc as required in organometallic chemistry is generally an expensive reagent because it is obtained from a costly reduction procedure. One of the best, but most expensive, procedures is the reduction of a dry zinc salt by metallic lithium or metallic potassium in an anhydrous organic solvent. The highly reactive zinc thus obtained has been extensively used in the literature, and the names of Rieke and his co-workers are definitively linked to the preparation of these active metals by reduction of salts with group I metals in organic solvents.[1,3,7]

It is probably difficult to obtain more active metals and it could be concluded that an alternative method is not needed. Although this conclusion is perhaps true for the synthetic organic chemist working in a research laboratory, environmental constraints must be taken into account for larger scale processes. Organic solvents and the use of metallic lithium as a reducing agent are certainly rather less environmentally friendly than water and electrons. In other words, active zinc obtained by chemical reduction of zinc salts in nonaqueous media does not fulfill the criteria of "green chemistry".

The only reduction of a zinc salt which does not generate a by-product is direct electrochemical reduction. This was the starting point for our efforts to develop a new method able to give metallic zinc (or other metals or alloys) directly. Good reagents in organometallic chemistry must be of high purity and fine granularity in order to obtain the highest possible surface/volume ratio. The metal obtained by our electrochemical method possesses both of these characteristics; this metal is produced electrochemically and ultrasound is used to expel the newly formed zinc crystals from the surface of the electrode and so prevent their further growth. The new method is of low cost with an absence of by-products, and allows the possibility of recycling the zinc salt obtained at the end of the reaction.

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Results and Discussion

The Sonoelectroreduction of Zinc Salts

It is well-known that the electroreduction of a zinc salt (or other metallic salts) on a cathode leads to metal deposition. Electrometallurgy is indeed the classical method for zinc preparation. If the current density is very high, the nucleation rate increases with respect to the growing rate and small crystals may be obtained instead of large deposits. The originality of the electroreduction we have developed[16][17] is essentially due to the use of out-of-phase pulses of high-density current and high-intensity pulsed pressure waves. A titanium-rod cathode forms part of an immersion horn activated by two piezoelectric ceramics and therefore also acts as an ultrasound emitter. During the electrical pulse, a large number of small metal nuclei are produced. The subsequent 20 kHz high-intensity ultrasound pulse expels the nuclei from the sonocathode, preventing the growth of the metal particles on the cathode surface. Furthermore, the ultrasound pulses clean the cathode surface (avoiding its passivation) and fully replenish the diffusion layer with metal cations by stirring the solution.[18] The metal particles so obtained are thus in a finely divided state with high surface areas and have a high degree of chemical purity. Consequently, this zinc powder is expected to exhibit a high degree of reactivity towards organic substrates. On the other hand, it must be noted that the sonoelectrochemical process is safe and environmentally friendly (the sonoelectroreduction is performed in an aqueous medium and requires only metal salts). It is cheap and easily reproducible (all parameters can be controlled and electricity is the cheapest reagent for the organic chemist). Another interesting feature of the pulsed sonoelectrochemical technique is its ability to control the size of the metal particles by modifying the electrochemical and ultrasound parameters.[17] All other parameters being constant, the shorter the electrical pulse duration, the smaller is the mean diameter of the metal nuclei and nanopowders are produced. High resolution transmission electron microscopy of zinc powders produced from a pure zinc sulfate bath with a current density of 2000 A/m^2 during pulses of 100 ms is shown in Figure 1. The particle size distribution curve reveals a mean diameter of about 50 nm together with larger agglomerates.

The electrical yield of zinc electrodeposition is always less than 100%. Hydrogen evolution takes place in agreement with thermodynamic studies.[19] Due to the strong agitation promoted by the ultrasound, oxygen degassing of the electrolyte is very effective. This dissolved oxygen is replaced by dissolved hydrogen generated during each electrochemical pulse which seems to prevent oxidation of the freshly prepared metal particles.

On the other hand, it is also possible to produce by sonoelectrochemistry zinc−copper alloys that are in a finely divided state. Indeed, the sonoelectroreduction of mixtures of Zn^{2+} and Cu^{2+} leads to fine Zn/Cu alloy powders with good electrical yields. The composition of the alloy produced by sonoelectrochemistry depends on the relative ratio of Zn^{2+} and Cu^{2+} in the electrolyte. Following this procedure, we obtained two Zn/Cu alloys one containing about 60% zinc to 40% copper and the other about 90% zinc to 10% copper. Finally, it must be observed that, per se, the sonoelectroreduction of metal salts is a very good way of minimising metal waste by recycling. Indeed, it is the metal cations resulting from the zero-valent metal consumed in organometallic reactions that are the starting material in ultrafine metal-powder production by sonoelectroreduction. This advantage of our new method will be illustrated at the end of this paper.

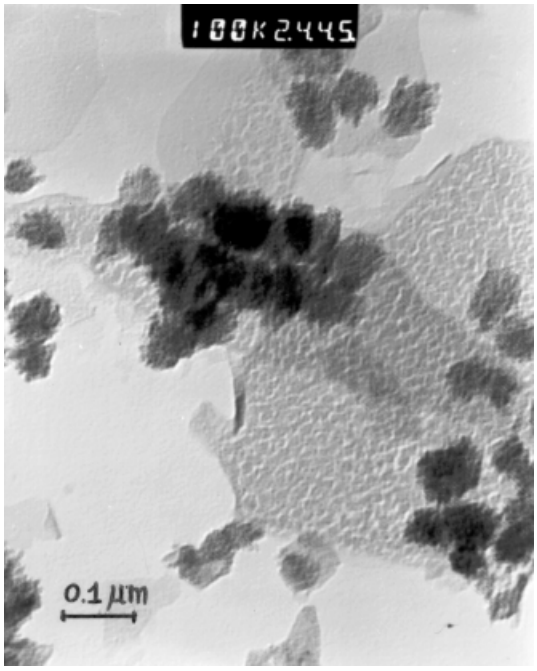


Figure 1. High resolution transmission electron microscopy of zinc nanopowder produced from a pure zinc sulphate bath

Examples of the Use of the Zinc Powder Obtained by Sonoelectroreduction in Organometallic Chemistry

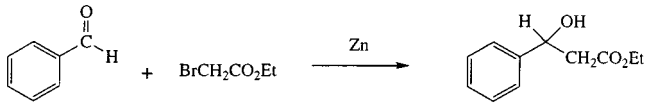
The examples which will be shown below correspond to well-known reactions leading to products already described. Our aim is only to show that, in many different cases, the zinc powder we obtain is comparable with the best active zinc available on the market and we are therefore confident that what can be exemplified with known reactions reactants and products would be also true for reactants and reactions that have not yet been studied. In all cases the yields which are given correspond to a quantitative analysis by NMR spectroscopy (and in many cases HPLC quantitative analysis) of the crude reaction mixture after elimination of the extraction solvent. In all cases, the reaction mixture was clean, containing the starting reactant(s) and the product(s) with less than 2% of noncharacterised contaminants. More details are given in the Experimental Section. The reactions used to demonstrate the efficiency or our new method for reactive zinc preparation were chosen in such a way as to have a large variety of different experimental

conditions, including reactions taking place in water and in organic solvents.

Reformatsky Reaction

The Reformatsky reaction of benzaldehyde with ethyl bromoacetate has been extensively studied in the literature.[20] Various activated zinc species have been used for this reaction. It is therefore possible to compare the reactivity of the zinc powder produced by our sonoelectrochemical method with others. From the results reported in Table 1, it is obvious that the zinc powder produced by sonoelectrochemistry is one of the most reactive forms known and is almost as reactive as Rieke zinc.

Table 1. Comparison of the reactivity of zinc powder produced sonoelectrochemically with other zinc species in the Reformatsky reaction



zinc variety	solvent	temp. (°C)	time (min.)	yield (%)
Rieke zinc	Et_2O	25	60	98[5]
Sonoelectroproduced zinc	**THF**	**25**	**60**	**92**
$ZnCl_2$ / Li / ultrasound	Et_2O	25	60	90[5]
Zn / Cu couple	THF	66	60	82[5]
commercial zinc dust	benzene	80	720	61[5]

Barbier Reaction

We have previously reported that zinc powder produced sonoelectrochemically exhibits a high degree of reactivity in the allylation of benzaldehyde in an aqueous medium.[16] This reaction was also performed in an organic solvent and can be efficiently extended to less-reactive substrates than benzaldehyde such as aliphatic ketones, acyl chlorides or even alkynes (Table 2).

The reaction with benzoyl chloride does not stop after the substitution of the chlorine atom since the more reactive carbonyl function is immediately involved in a subsequent reaction with allyl bromide. On the other hand, allyl chloride, which is usually a poor reagent in organozinc chemistry compared to allyl bromide, reacts with benzaldehyde in the presence of zinc powder produced by sonoelectrochemistry, even in an aprotic solvent (Table 3).

However, the behaviour is different in an aqueous medium. In this latter case, the reaction proceeds via a "one-electron transfer" mechanism.[2] Similar reactivities can therefore be predicted for chloride and bromide since the

Table 2. Barbier allylation in THF with sonoelectroproduced zinc

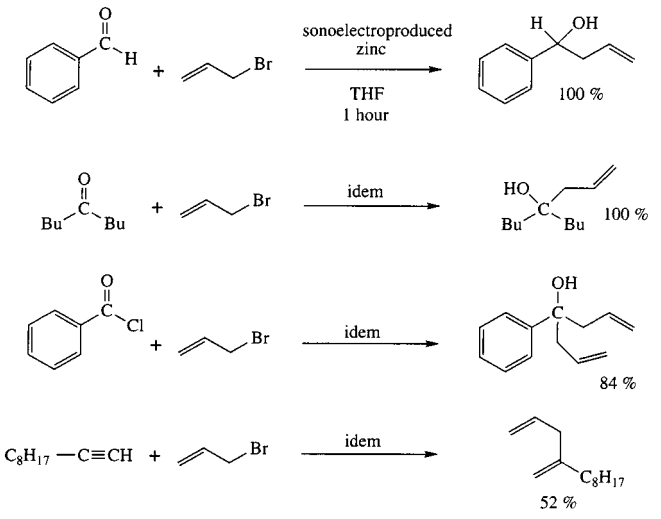
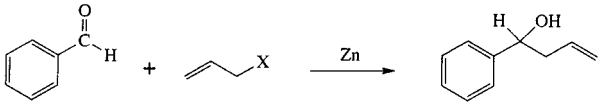


Table 3. Effect of the reaction medium and the nature of the halide for the allylation of benzaldehyde in the presence of sonoelectroproduced zinc



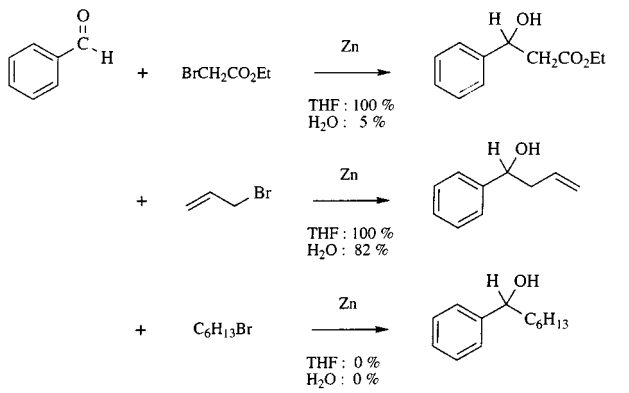
reaction conditions	yields
X = Cl , THF, 16 hours	100 %
X = Cl , THF, 1 hour	8 %
X = Cl , H_2O-NH_4Cl (2M), 1 hour	68 %
X = Br , THF, 1 hour	100 %
X = Br , H_2O-NH_4Cl (2M), 30 minutes	88 %

rate-determining step seems to be the electron transfer from zinc to the organic halide. On the other hand, classical organometallic reactions in aprotic solvents strongly depend on chelation and are therefore very sensitive to the nature of the halogen atom.

Reactivity differences in THF and water as solvents are also observed when various bromo-derivatives reacting with benzaldehyde are compared (Table 4). In THF, the mechanism probably implies the formation of a true C−Zn bond and shows the classically poor reactivity of alkyl bromide with respect to allyl bromide or ethyl bromoacetate. In water, allyl bromide is the only derivative of the series which can react in a significant way.

The lack of reactivity of alkyl bromides in THF or water has already been described in the literature[13] with pure zinc as reagent. In this case, the superiority of Rieke zinc for carbonyl compounds alkylation is obvious.[7]

Table 4. Comparison of the reactivity of some bromide reagents in aqueous and aprotic media for the Barbier reaction with benzaldehyde (reaction time: 1 hour)



Alkyne Reduction

The chemo- and stereoselective reduction of α-hydroxy alkynes has been reported in the literature.[22] We performed these reductions in order to compare once again the reactivity as well as the chemo- and stereoselectivity of sonoelectrochemical zinc with those of highly active Rieke zinc. Zinc powder produced by the new method reduces α-hydroxy alkynes with a degree of efficiency, a chemospecificity and a stereoselectivity similar to Rieke zinc (Table 5).

Table 5. Reduction of α-hydroxy alkynes with zinc powder produced by sonoelectroreduction: reactivity, and chemo- and stereoselectivity

a) R1 = CH2 − CH3 ; R2 = H ; R3 = Et

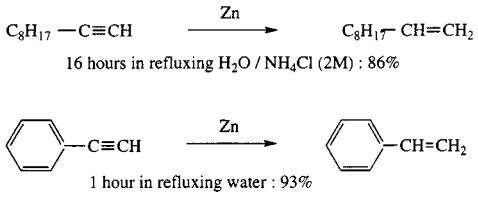
	yield	cis/trans
Rieke zinc, THF/MeOH/H_2O (7/5/1), reflux, 40 hours [9]	85%	19/1
Sonoelectroproduced zinc, THF/MeOH/H_2O (7/5/1), reflux, 40 hours	92%	>9/1
Sonoelectroproduced zinc, H_2O/NH_4Cl (2M)/HCl (pH=2.8), reflux, 16 hours	100%	8/2
Sonoelectroproduced zinc, distillated water, reflux, 16 hours	100%	9/1

b) R_1 =  ; R_2 = Me ; R_3 = Et

	yield	cis/trans
Rieke zinc, THF/MeOH/H_2O (7/5/1), reflux, 4 hours [9]	58%	3/1
Sonoelectroproduced zinc, THF/MeOH/H_2O (7/5/1), reflux, 4 hours	40%	4/1
Sonoelectroproduced zinc, H_2O/NH_4Cl (2M)/HCl (pH=2.8), reflux, 2 hours	100%	1/1
Sonoelectroproduced zinc, distillated water, reflux, 2 hours	43%	3/1

Furthermore, it appears that the use of aqueous systems increases the reaction rates. Nevertheless, the resulting α-hydroxy alkenes can isomerize in acidic aqueous systems. Reaction conditions must therefore be carefully chosen in order to optimize the rate/stereoselectivity balance of the reduction. In this context, distilled water seems to be a good compromise. The reaction can be easily extended to simple aromatic and aliphatic alkynes (Table 6). The aqueous reduction with sonoelectrochemically produced zinc powder is accordingly a general, safe, easy, smooth and chemoselective method to reduce triple bonds to double bonds with high stereoselectivity.

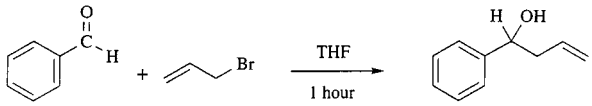
Table 6. Reduction of aromatic and aliphatic alkynes with zinc powder produced by sonoelectroreduction



Reactivity of Zinc−Copper Alloys

The sonoelectroreduction of salt mixtures is a simple method of preparing metal alloys at room temperature. Since sonoelectroreduction can be used to prepare alloys of various compositions we decided to test the relationship between the copper−zinc content of the alloys and their reactivity in a very typical Barbier reaction (Table 7). Since copper is ineffective in this reaction, it is normal to observe a significant rate decrease as soon as the amount of copper becomes appreciable. More interesting is the acceptable reactivity decrease observed with a 90/10 zinc−copper alloy and the possibility of seeing whether the decrease in reactivity is associated with an increase in selectivity. This was tested in the case of two different reactions, namely a reductive dehalogenation[23] (which can give mono- and didehalogenated products) and a competitive allylation starting from a 1/1 mixture of an aldehyde and a ketone (Table 8). The rate decrease, acceptable in all cases, is associated with a selectivity increase, but the change is not sufficient to be of great importance in organic synthesis.

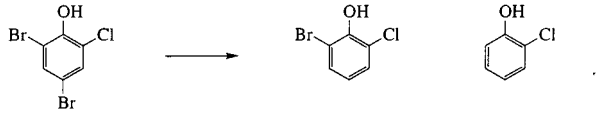
Table 7. Reactivity of sonoelectroproduced zinc-copper alloys and pure metals in the allylation of benzaldehyde



metal species	yield	comments
pure zinc	100 %	reaction completed within the first 10 minutes
Zn/Cu (90/10)	100 %	reaction completed within the first 30 minutes
Zn/Cu (60/40)	23 %	
pure copper	0 %	

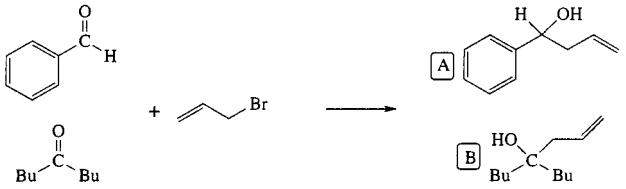
Table 8. Effect of the sonoelectroproduced alloy composition for reductive dehalogenation and benzaldehyde allylation

Reductive dehalogenation



Pure zinc	49	49
Zn/Cu alloy (90/10)	56	42
Zn/Cu alloy (60/40)	65	26

Competitive allylation



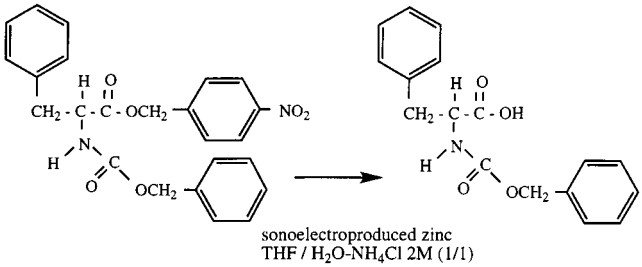
	yield in A	yield in B	A/B
Pure zinc	100%	13%	7.7
Zn/Cu alloy (90/10)	91%	6%	15.2
Zn/Cu alloy (60/40)	63%	3%	21

Metal Waste Recycling

As discussed in the introduction, the recycling of zinc salts at the end of the reduction of the organic substrate is a major challenge and chemists, even those working in research laboratories, are more and more concerned by this problem. Obviously, the method described here for zinc preparation provides the opportunity for recycling the zinc salts generated by organometallic reactions using an electric current as the only source of electrons. Recycling metal waste can be considered in two different ways. On the one hand, it might be possible to re-use the cationic zinc species obtained after the organometallic reaction for the sonoelectrolytic production of the zinc powder as a distinct step. However, on the other hand, it would be more interesting to establish an in situ catalytic recycled system. Thus, we decided to test this stategy on the cleavage of *p*-nitroesters with zinc.[24]

We found first that it was possible to perform the in situ ester cleavage of cbz-*p*-NO_2-benzylphenylalanine. This corresponds to the sonoelectroproduction of the zinc powder in the presence of the *p*-NO_2-benzyl ester, which is electrochemically inert in the electrolysis conditions in the absence of zinc salts but which is fully cleaved after 90 minutes of electrolysis in the presence of zinc salts.

Nevertheless, we did not succeed in performing the process catalytically. Furthermore, the electrolyte solution did not resist for a long time, probably due to a THF degradation. In order to solve the metal waste recycling problem we were obliged to apply an alternative procedure. The *p*-NO_2-benzyl ester in THF was added to a zinc powder suspension previously obtained by the sonoelectroreduction of an aqueous electrolyte (NH_4Cl 2 M and $ZnCl_2$ 0.24 M). After being stirred for 30 minutes, the reaction mixture was extracted twice with dichloromethane and the aqueous phase directly re-used in subsequent zinc powder sonoelectroproduction and organometallic reaction steps. In this way, we performed six quantitative ester cleavages with the same electrolyte and without any significant loss of zinc cations (<15%, determined by colorimetric titration of Zn^{2+} by dithizone).



Conclusions

The sonoelectrochemical reduction of metal salts in water appears to be an interesting alternative to conventional methods for reactions in organozinc chemistry. Indeed, zinc powders produced by sonoelectrochemistry are generally highly reactive. Furthermore, the process is safe, cheap and easy to control, and it is possible to recycle the metal salts produced during the reaction. As we have previously shown, the sonoelectrochemical method described here is not limited to the production of zinc. Moreover, it can be performed in solvents other than water. Many other metals, oxides and even semi-conductors can be produced as very fine powders and with a very high degree of purity by this technique.[25] Considering the importance of heterogeneous liquid−solid reactions in organic synthesis where the solid can be a reactant (as illustrated in this paper) or a catalyst, the method described here may have many other applications in synthetic organic chemistry. Applications in material sciences are also under study in our laboratories.

Experimental Section

Sonoelectrochemical Process for the Production of Ultrafine Zinc Powder: The sonoelectrochemical device has been described previously.[16] In a typical procedure a mixture of zinc chloride (8 g) and ammonium chloride (supporting electrolyte, 26 g) in water (250 mL) was subjected to a pulsed electric current (current density = 8000 A/m^2; pulse duration = 300 ms) and pulsed pressure waves (ultrasound intensity above the cavitation threshold; pulse duration = 100 ms followed by a dead time of 200 ms) for one hour with the two irradiation periods out of phase. The resulting suspension was filtered under argon on a 0.1 μm Millipore filter,

washed with water, rinsed thoroughly with anhydrous THF and dried under an argon flux, affording 613 mg of finely divided zinc powder (electrical yield = 67%). The electrolysis could be extended for longer periods in order to produce larger amounts of zinc powder. High-resolution transmission electron microscopy pictures of the obtained zinc powder showed that most of the metal particles were submicronic (around 500 nm) (see Figure 1).

Sonoelectrochemical Process for the Production of Zinc−Copper Alloys: The sonoelectroreduction (electrical and ultrasonic parameters described in the typical procedure reported above) of an electrolyte containing $CuSO_4 \cdot 5H_2O$ (6 g/L); $ZnCl_2$ (33 g/L) and NH_4Cl (107 g/L) gave a Zn/Cu alloy for which the composition, determined by Energy Dispersive X-ray analysis, was about 60% of zinc and 40% of copper (electrical yield = 92%). In a similar manner, a Zn−Cu alloy containing about 90% of zinc and 10% of copper was obtained by changing the $CuSO_4 \cdot 5H_2O$ concentration (2 g/L; electrical yield = 71%). The alloy powders were shown to be true solid solutions and not simple mixtures of zinc and copper or copper cementation on the zinc particles by X-ray diffraction.

Procedure for the Reformatsky Reaction of Benzaldehyde: Benzaldehyde (848 mg, 8 mmol) and ethyl bromoacetate (1670 mg, 10 mmol) in 10 mL THF were added to zinc powder (982 mg, 15 mmol) in 10 mL THF under a nitrogen atmosphere at room temperature. The resulting mixture was stirred for one hour, diluted in water and extracted twice with dichloromethane. The concentration in vacuo of the organic phases gave 1600 mg of an oil (100% reaction yield based on an NMR spectroscopic analysis {at 250 MHz} of the relative integrations of the aldehydic proton for benzaldehyde and the proton on the carbon bearing the hydroxy group for the hydroxy ester). Flash chromatography (CH_2Cl_2/silica gel) of the crude mixture gave 1428 mg of the expected product (92% isolated yield).

General Procedure for the Barbier Reaction in THF: The corresponding electrophilic substrate (8 mmol, see Tables 2,3 or 4) and the halide reagent (10 mmol) in THF (10 mL) were added to zinc powder (982 mg, 15 mmol) in THF (10 mL) under a nitrogen atmosphere at room temperature. The resulting mixture was stirred for one hour, diluted in water and extracted twice with dichloromethane. Evaporation of the solvent under vacuum gave the crude reaction mixture which was analysed by ^{1}H NMR spectroscopy and HPLC.

General Procedure for the Barbier Reaction in an Aqueous Solvent: The corresponding electrophilic substrate (8 mmol, see Tables 2,3 or 4) and the halide reagent (10 mmol) in THF (10 mL) were added to zinc powder (982 mg, 15 mmol) in H_2O/NH_4Cl (20 mL, 2 M) at room temperature. The resulting mixture was stirred for one hour, diluted with water and extracted twice with dichloromethane. Concentration of the organic phases under vacuum gave the crude reaction mixture which was analysed by ^{1}H NMR spectroscopy and HPLC.

General Procedure for the Reduction of Alkynes: Zinc powder (1000 mg, 15 mmol) and the corresponding alkyne (5 mmol) were refluxed in the solvent system described in Table 6 or 7. The resulting mixture was then diluted with water, extracted twice with ether and dried over $MgSO_4$. Concentration of the organic phases under vacuum gave the crude reaction mixture which was analysed by ^{1}H NMR spectroscopy.

Procedure for the Basic Dehalogenation of Compound 2: Compound **2** (3 mmol) and zinc powder (1 g, 15 mmol) were reacted in H_2O/NaOH (10 mL of a 10% solution) at room temperature for two hours. The resulting mixture was then diluted with water, acidified with HCl, extracted twice with ether and dried over $MgSO_4$. Concentration in vacuo of the organic phases gave a mixture of the dehalogenated products which was analysed by ^{1}H NMR spectroscopy and HPLC.

Procedure for the Competitive Allylation of Benzaldehyde and 5-Nonanone: Benzaldehyde (8 mmol), 5-nonanone (8 mmol) and allyl bromide (1210 mg, 10 mmol) in THF (10 mL) were added to 15 mmol of the metal species in 10 mL THF under a nitrogen atmosphere at room temperature. The resulting mixture was stirred for one hour, diluted with water and extracted twice with dichloromethane. Concentration in vacuo of the organic phases gave the crude reaction mixture which was analysed by ^{1}H NMR spectroscopy.

Procedure for the In Situ Ester Cleavage of Compound 3: A mixture of the ester (2 mmol) in THF/H_2O (60 mL), and $(NH_4)_2SO_4$ (0.32 M) and $ZnSO_4 \cdot 7H_2O$ (0.22 M) (1/1) was subjected to pulsed electrolysis (parameters described above in the sonoelectrochemical process; platinum counter-electrode). The evolution of the reaction was followed by HPLC.

Acknowledgments

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