

# Facile Preparation of Highly Reactive Electrogenerated Zinc

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## Abstract

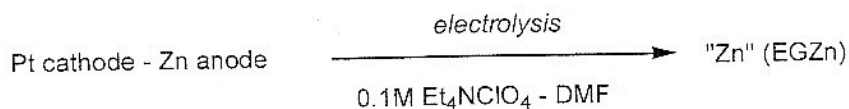
Highly reactive electrogenerated zinc metal (EGZn/Naph) was readily prepared by electrolysis of a DMF solution containing naphthalene and a supporting electrolyte in a one-compartment cell fitted with a platinum cathode and a zinc anode. The reactivity of this EGZn/Naph was elucidated by an efficient transformation of ethyl 2-bromobutanoate as a model substrate into the corresponding organozinc compound, which can not be achieved by the use of usual zinc metal. It was found that the electrolysis at -10 °C at a constant current of 60 mA/cm<sup>2</sup> under nitrogen atmosphere was the optimum conditions in preparing this EGZn/Naph.

**Keywords:** electrolysis, reactive zinc, naphthalene, organozinc compound

## Introduction

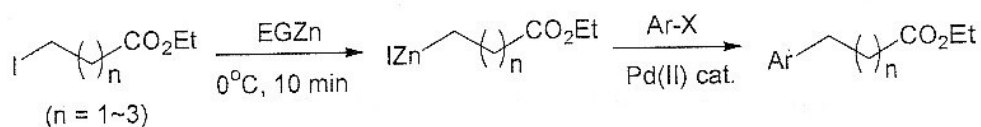
Organozinc compounds are very useful organometallic compounds for the forming reaction of carbon-carbon bonds [1]. Organozinc halides can usually be prepared by direct insertion of zinc metal into organic halides [2], but commercially available zinc metal is generally poorly reactive. Therefore, activation of the metal is necessary for preparation of organozinc halides. Various method of zinc activation, such as the reduction of zinc halide with alkaline metal or alkali metal naphthalenide, have been reported [3]. These methods, however, require high temperature and long reaction times, or vigorous stirring during the reaction.

We previously reported a new method for preparation of reactive zinc by electrolysis of a DMF solution containing 0.1M Et<sub>4</sub>NClO<sub>4</sub> with a platinum cathode and a zinc anode (Scheme 1) [4].



**Scheme 1**

It was shown that this electrogenerated reactive zinc (EGZn) was an aggregation of very fine crystalline zinc particles with a large surface area [5]. It was very reactive and was successfully used in isoprenylation [4] and allylation [5, 6] of aldehydes and ketones. We have also reported a facile preparation of organic compounds from functionalized alkyl iodides by using EGZn and their cross-couplings with aryl halides (Scheme 2) [7]. However, organozinc bromides were rarely



Scheme 2

obtained or were only obtained in very low yields from the corresponding organic bromides, even if the reactive EGZn was used.

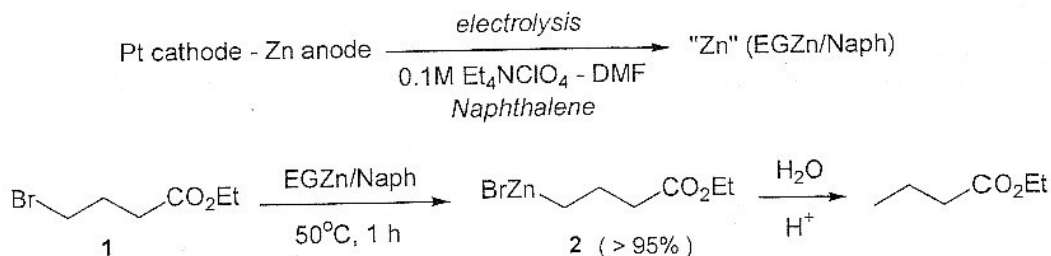
On the other hand, electrochemical reduction of polyaromatic compounds gives the corresponding polyaromatic radical anion, which can efficiently reduce alkyl or aryl halide [8]. It has been also reported that metal halides such as magnesium [9] or copper halides [9] were reduced by lithium or sodium naphthalenide. Zero valent metal prepared by this method reacts with various organic compounds to give the corresponding organometallic compounds.

Transformation of ethyl 4-bromobutanoate which is used as a model substrate into the corresponding organozinc compound proceeded only in a 37% yield when EGZn was used. Therefore a new method for the preparation of more highly reactive zinc was desired in order to pursue more efficient transformation of organic bromides into the corresponding organozinc reagents. As a result of several attempts, we have developed a new electrochemical method for the preparation of more highly reactive zinc (EGZn/Naph) by using naphthalene as a mediator. In this paper, the author describes the preparation and reactivity of this highly reactive zinc.

### Result and Discussion

Several attempts had been done in order to find out the optimum conditions for the reaction of ethyl 4-bromobutanoate with EGZn/Naph. As a result, EGZn/Naph (6 mmol) was readily prepared by electrolysis of a DMF (15 ml) solution containing naphthalene (2 eq) and 0.1M  $\text{Et}_4\text{NClO}_4$  in a one-compartment cell fitted with a platinum plate cathode ( $2 \times 2 \text{ cm}^2$ ) and a zinc plate anode ( $2 \times 2 \text{ cm}^2$ ). Electrolysis at  $-10^\circ\text{C}$  at a constant current of  $60 \text{ mA/cm}^2$  in a nitrogen atmosphere was found to give highly reactive zinc which could transform ethyl 4-bromobutanoate (1) into the corresponding organozinc compound (2) in almost quantitative yield (Scheme 3).

Yield of the transformation was monitored by GC and was determined by the disappearance of ethyl 4-bromobutanoate and also by the formation of protonated compound after hydrolysis of the organozinc bromide with diluted HCl solution (Scheme 3).



Scheme 3

The reactivity of EGZn/Naph in the forming reaction of organozinc bromide 2 from ethyl 4-bromobutanoate 1 was compared with the reactivities of other zinc metals. The results are summarized in Table 1. These results show that the use of commercially available zinc or EGZn with the addition of naphthalene was not effective in terms of reactivity and that the presence of

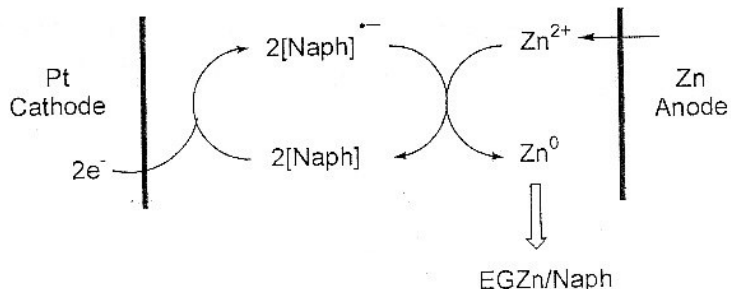
naphthalene molecules in the electrochemical reduction step is required for preparation of much higher reactive zinc.

Table 1. Transformation of Bromoester 1 to Organozinc 2 under Various Conditions<sup>a)</sup>

Zn	Temperature (°C)	Time (h)	Conversion of 1 (%) <sup>b)</sup>
Zn + Naph <sup>c)</sup>	r.t.	18	0
Zn + Naph <sup>c)</sup>	70	3	0
EGZn + Naph <sup>d)</sup>	r.t.	3	37
EGZn/Naph	r.t.	1	95

- a) Ethyl 4-bromobutanoate (1) (5 mmol) was reacted in DMF (10 ml) with zinc metal (6 mmol).  
 b) Determined by GC analysis.  
 c) Commercially available Rare Metallic zinc (6 mmol) in the presence of naphthalene (12 mmol) was used.  
 d) EGZn (6 mmol) in the presence of naphthalene (12 mmol) was used.

Probable reaction pathway for the formation of EGZn/Naph is shown in Scheme 4. At the cathode, a one-electron reduction of naphthalene molecule readily occurred to give naphthalene radical anion preferentially. The formation of the naphthalene radical anions was shown by the dark green color which appeared on the surface of the cathode. On the other hand, at the anode, dissolution of the zinc metal occurred to give zinc ions, which were reduced by the naphthalene radical anions to give zero-valence EGZn/Naph. However, the true nature and structure of this EGZn/Naph are not clear at the present stage, but it was found to be very reactive towards an oxidative addition to organic bromides.



Scheme 4

## Conclusion

We developed a new electrochemical method for the preparation of highly reactive zinc (EGZn/Naph) by using naphthalene as a mediator in the electrolysis. The corresponding organozinc bromide could readily be prepared under mild conditions by the reaction of ethyl 4-bromobutanoate with EGZn/Naph. Subsequent cross-coupling reaction of the organozinc bromide thus prepared with iodobenzene readily took place in the presence of a palladium catalyst to give the corresponding cross-coupled products, ethyl 4-phenylbutanoate in 96% of isolated yields.

### Acknowledgement

This work was supported by a Grant-in-Aid for Scientific Research (B) (No. 11450342) from Ministry of Education, Science, Sports and Culture.

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