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Mechanochemical Reaction of Aromatic Ketones and Aldehydes in the Presence of Zn–$ZnCl_2$

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Abstract: The solvent-free reactions of aromatic ketones and aldehydes in the presence of Zn-$ZnCl_2$ were performed with the aid of high-speed vibration mill, Retsch MM200 mixer mill and Retsch RM100 mortar grinder to give pinacol coupling and reduction products in varying yields.

Keywords: Pinacol coupling, solvent-free reaction, aromatic ketones, aromatic aldehydes, mechanochemical reaction.

The pinacol coupling[1] is one of the most powerful methods for constructing carbon-carbon bond. Generally, this reaction is carried out by treatment of carbonyl compounds with appropriate metal reagent and/or metal complex to give vicinal diols. A number of different types of metal reagents have been used. Among them, metallic zinc is a cheap and efficient reagent, Zn in NH_4Cl (aq)-THF solution[2], Zn in dilute hydrochloric acid[3], Zn-NaOH in methanol[4], as well as Zn-$ZnCl_2$ both in THF-H_2O solution and in the solid state[5] have been reported.

Compared with the organic liquid or aqueous media reactions, solvent-free reaction has the advantages in low cost, less toxicity and easy handling and thus attractive to chemists, especially from the viewpoint of green chemistry[6]. Various solvent-free reactions were found to occur by hand grinding[7]. More recently, mechanical milling was employed to activate organic reactions[8], especially in fullerene chemistry[9]. However, more knowledge needs to be accumulated to fully understand mechano- chemical reactions by different mechanical activation methods. Herein we report the mechanochemical reaction of aromatic ketones and aldehydes in the presence of Zn-$ZnCl_2$ by three different mechanical activation techniques: high-speed vibration mill, Retsch MM200 mixer mill and Retsch RM100 mortar grinder.

The high-speed vibration milling (HSVM) was first applied to the solvent-free Reformatsky-type reaction of C_{60} in 1996[10]. A mechanochemical reaction by HSVM is done in a home-made vibration mill at a vibration frequency of 3500 cycles per minute, the details have been described previously[11]. Even though this technique has been extended to several different kinds of fullerene reactions[9,12], there is no report on mechanochemical reaction of nonfullerene compound by HSVM. The coupling reactions of aromatic

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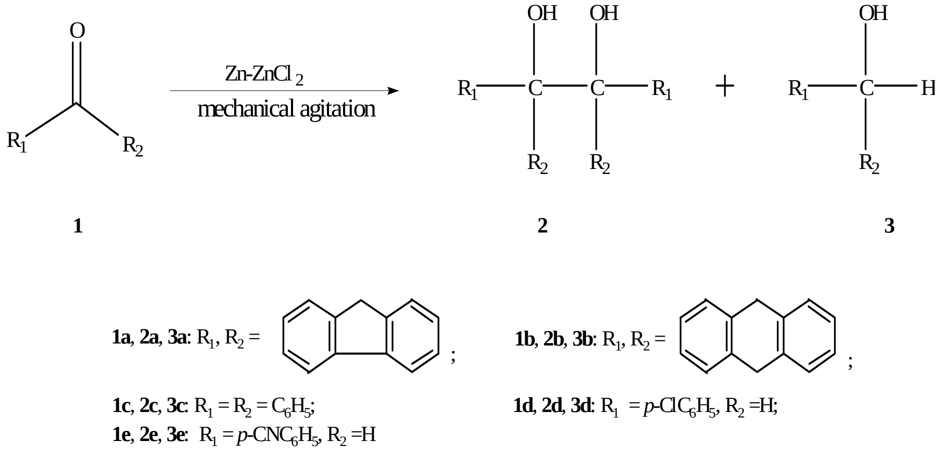
ketones and aldehydes in the presence of Zn-$ZnCl_2$ were chosen for our HSVM study in order to compare the reaction behaviors under different conditions because these reactions have been examined both in aqueous solution and in the solid state by hand grinding[5].

A typical procedure for the coupling reaction of 9-fluorenone (**1a**) in the presence of Zn-$ZnCl_2$ is as follows: a mixture of **1a** (18 mg, 0.1 mmol), Zn powder (65 mg, 1.0 mmol, treated with 1 mol/L HCl to remove the oxide on its surface) and $ZnCl_2$ (13.6 mg, 0.1 mmol) was vigorously milled for 30 min, then the reaction mixture was treated with 3 mol/L HCl (5 mL), extracted with ethyl acetate (3 × 10 mL). The condensed organic extract was separated on a silica gel column with petroleum ether/ethyl acetate as the eluent to give pure coupling product **2a** (11 mg, 61%) and reduction product **3a** (4.5 mg, 25%). The same procedure for the HSVM reaction of anthrenone (**1b**), benzophenone (**1c**), *p*-chlorobenzaldehyde (**1d**), *p*-cyanobenzaldehyde (**1e**) in the presence of Zn-$ZnCl_2$ afforded the corresponding coupling and reduction products (**Scheme 1**).

Scheme 1



The yields and reaction times for the coupling and reduction products of aromatic carbonyl compounds **1a-e** in the presence of Zn-$ZnCl_2$ under HSVM conditions are listed in **Table 1**.

To see how activation methods affect the reaction behavior, the above reactions were performed on a Retsch MM200 mixer mill and a Retsch RM100 mortar grinder.

Table 1 Yields and reaction times for the coupling and reduction products of **1a-e** in the presence of Zn-$ZnCl_2$ under HSVM conditions

Compound	Time (min)	Yield of **2** (%)	Yield of **3** (%)
1a	30	61	25
1b	30	57	28
1c	30	41	15
1d	30	20	10
1e	30	50	0

The Retsch MM200 mixer mill can be operated at variable vibration frequency, and was set at 1800 cycles per minute for our experiments. The Retsch RM100 mortar grinder is working much slower and is operated at 90 rpm with pressure setting at 1, and requires more amount of samples. The amount of carbonyl compound was 0.2 mmol and 10 mmol for the Retsch MM200 mixer mill and Retsch RM100 mortar grinder, respectively.

The yields and reaction times for the coupling and reduction products of aromatic carbonyl compounds **1a-e** in the presence of Zn-$ZnCl_2$ under Retsch MM200 mixer mill and Retsch RM100 mortar grinder conditions are collected in **Table 2** and **Table 3**, respectively.

It can be seen from **Tables 1-3** that the yields and relative ratios of the pinacol coupling product and reduction product of the aromatic ketones and aldehydes under both HSVM and Retsch MM200 mixer mill conditions are comparable, while the yield and selectivity of the pinacol coupling product are much higher under the Retsch RM100 mortar grinder conditions. The vibration frequencies of HSVM and Retsch MM200 mixer mill have no obvious effect on the product distribution. For the mechano- chemical reaction of **1a**, **1c**, **1e** by Retsch RM100 mortar grinder, only pinacol coupling product was obtained. The less favored yield and selectivity of coupling product by both HSVM and Retsch MM200 mixer mill techniques is probably due to less favored coupling process between two carbonyl radical anions and the instability of the coupling under these more vigorous milling conditions. The latter is evidenced by the fact that milling of **2b** by HSVM for 30 min resulted in partially decomposition into **1b** and **3b**. The observation of product decomposition and association-dissociation equilibrium has been noted in mechanochemical reactions of C_{60} by HSVM technique[11]. Among the three techniques, the results from the mechanochemical reactions of aromatic ketones and aldehydes by Retsch RM100 mortar grinder are most close to those by hand grinding[5].

Table 2 Yields and reaction times for the coupling and reduction products of **1a-e** in the presence of Zn-$ZnCl_2$ under Retsch MM200 mixer mill conditions

Compound	Time (min)	Yield of **2** (%)	Yield of **3** (%)
1a	60	66	28
1b	60	58	28
1c	60	60	21
1d	60	24	13
1e	60	57	0

Table 3 Yields and reaction times for the coupling and reduction products of **1a-e** in the presence of Zn-$ZnCl_2$ under Retsch RM100 mortar grinder conditions

Compound	Time (min)	Yield of **2** (%)	Yield of **3** (%)
1a	60	90	0
1b	60	79	9
1c	60	88	0
1d	60	73	14
1e	60	89	0

In conclusion, the mechanochemical reaction of aromatic ketones and aldehydes in the presence of Zn-$ZnCl_2$ under the high-speed vibration mill, Retsch MM200 mixer mill and Retsch RM100 mortar grinder conditions have been found to give pinacol coupling product and reduction product in varying yields. Among the three activation methods, the more gentle Retsch RM100 mortar grinder technique afforded much higher yield and selectivity of the pinacol coupling product.

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References

1. B. E. Khan, R. D. Rieke, *Chem. Rev.*, **1988**, *88*, 733.
2. L. Wang, X. Sun, Y. Zhang, *J. Chem. Res. (S)*, **1998**, 336.
3. X. Liu, Y. M. Zhang, *Chin. J. Org. Chem.*, **2003**, *23*, 92.
4. S. M. Liu, J. T. Li, Y. J. Bian, J. H. Yang, T. S. Li, *Chin. J. Org. Chem.*, **2002**, *22*, 675.
5. K. Tanaka, S. Kishigimi, F. Toda, *J. Org. Chem.*, **1990**, *55*, 2981.
6. P. T. Anastas, J. C. Warner, *Green Chemistry: Theory and Practice*, Oxford, **1998**.
7. K. Tanaka, F. Toda, *Chem. Rev.*, **2000**, *100*, 1025.
8. J. F. Fernández-Bertrán, *Pure Appl. Chem.*, **1999**, *71*, 581.
9. K. Komatsu, Y. Murata, G. W. Wang, *et al.*, *Fullerene Sci. Technol.* **1999**, *7*, 609.
10. G. W. Wang, Y. Murata, K. Komatsu, T. S. M. Wan, *Chem. Commun.*, **1996**, 2059.
11. K. Komatsu, G. W. Wang, Y. Murata, *et al.*, *J. Org. Chem.*, **1998**, *63*, 9358.
12. For a most recent example, see: G. W. Wang, T. H. Zhang, E. H. Hao, L. J. Jiao, Y. Murata, K. Komatsu, *Tetrahedron*, **2003**, *59*, 55.

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