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Facile Synthesis of Ferrocenylenones in Free Solvent at Room Temperature

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Abstract: The rate of formation of aldol condensation products by being ground acetylferrocene and various aromatic aldehydes without solvent was dramatically enhanced comparing to the conventional methods. The yield is high (84 % - 96 %) at room temperature.

Keywords: Acetylferrocene, ferrocenylenones, solid state, grind.

Ferrocenylenones are important intermediate compounds in organic synthesis[1]. The chemistry of hetero- and carbocycles with ferrocenyl substituents is based on sufficiently high accessibility of the starting material-α, β-unsaturated carbonyl compounds of the ferrocene series[2]. The derivatives of ferrocene have attracted the attention of scientists all over the world because of their numerous applications in chemical sensing, asymmetric catalysis, material science and medical chemistry[3,4]. Claisen-Schmidt reaction of acetylferrocene **1** has been paid much attention in the past years, which is usually performed under classical homogeneous conditions in ethanol[5,6]. In 1990, Toma and collaborators described the synthesis of such products under phase-transfer conditions using 18-crown-6 ether as catalyst[7].

Many solid phase organic synthesis (SPOS) were reported[8,9]. These reaction have a series of advantages, such as reduced pollution, low cost, mild conditions and simplicity of working up[10]. Toda *et al*. reported a series of SPOS such as the aldol reactions in free of solvent[8]. Recently Villemin *et al*. reported the synthesis of ferrocenylenones (yield 53 % - 92 %) using powdered KOH as base without solvent in the presence of a phase-transfer catalyst (PTC), at room temperature, or under microwave irradiation[11]. In view of green chemistry, it is necessary to develop new methods which are simple and environmentally friendly for the synthesis of ferrocenylenones. Herein, we have investigated the synthesis of ferrocenylenones using pulverized KOH or NaOH as base without solvent at room temperature by being ground. These results are concluded in **Scheme** and **Table 1**.

As shown in **Table 1**, it was found that the condensation of acetylferrocene **1** with aromatic aldehydes **2-11** gave the corresponding ferrocenylenones **12-21** in high yields

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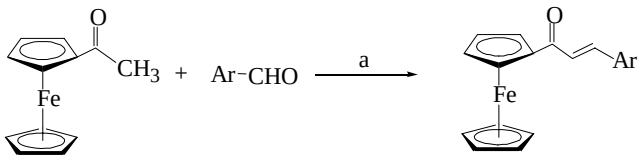
Scheme



1 **2-11** **12-21**

a) KOH , rt., Free solvent

Table 1 The reaction of aromatic aldehyde with acetylferrocene in the presence of pulverized potassium hydroxide [a]

Compd.	Ar-CHO	Products	Time/min.	Yield / %[b]	mp. (°C)[d]	
					Obtained	Reported[11,12]
2	C_6H_5CHO	**12**	10	90	137-138	139-140
3	*p*-$CH_3C_6H_5CHO$	**13**	5	96	173-174	
4	*p*-$OCH_3C_6H_5$	**14**	25	90	153-154	153-154
5	*p*-$NO_2C_6H_5$[c]	**15**	25	90	192	
6	*p*-ClC_6H_5	**16**	15	90	161-162	160-161
7	*o*-ClC_6H_5	**17**	25	80	104-105	
8	furaldehyde	**18**	10	84	155-156	155-157
9	2-thienylcarboxaldehyde	**19**	10	90	146-147	146-147
10	heliotropin	**20**	16	93	167-168	169-170
11	2-Pyridinecarboxaldehyde[c]	**21**	7	91	152-153	152-153

[a] All experiments carried out in solid state at room temperature. [b] Isolated yields. [c] Substance **1**:**5** =1:1.2 mol and substance **1**:**11** = 1:1.1 mol. [d] All the melting points are uncorrected.

Table 2 The reaction of aromatic aldehyde with acetylferrocene in the presence of pulverized sodium hydroxide.[a]

Compd.	Ar-CHO	Products	Time/min.	Yield / %[b]
2	C_6H_5 CHO	**12**	10	84
3	*p*-$CH_3C_6H_5$ CHO	**13**	5	88
4	*p*-$CH_3OC_6H_5$	**14**	25	83
5	*p*-$NO_2C_6H_5$	**15**	30	74
6	*p*-ClC_6H_5	**16**	15	83
7	*o*-ClC_6H_5	**17**	25	84

[a] All experiments carried out in solid state at room temperature. [b] Isolated yields.

under above conditions. To obtain the desired products **13**, **21** with **3, 11** and **1**, only 5, 7 min was needed and yields were high (96, 91 %, respectively).

In order to compare the effect of the additive, NaOH and LiOH were used. It was

found that powdered NaOH was another efficient base in the aldol reactions (**Table 2**). But, it was not as good as the pulverized KOH in the reaction of **1** with **2-7**. organic layer was washed with water (20 mL×2) and dried over anhydrous magnesium sulfate. Evaporation of solvent under reduced pressure gave the residue which was further purified by recrystallization using hexane / ethyl acetate (4:1).

In summary, we have developed a mild method for synthesis of ferrocenylenones **12-21** from **1** in solvent free condition in the presence of pulverized KOH by being ground. This method is not only more rapid and efficient than others, but also in accord with green chemistry. The mechanism of aldol reactions in solid state is being researched in our laboratory.

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