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Aldol Condensation of Acetylferrocene under Ultrasound

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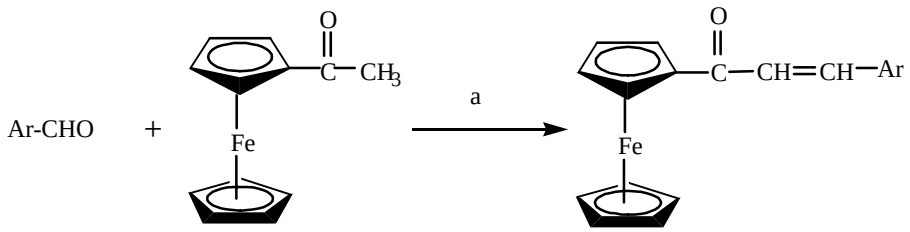
Abstract: Aldol condensation of acetylferrocene with aromatic aldehydes afforded ferrocenylenones in 76%-92% yields under ultrasound at room temperature.

Keywords: Acetylferrocene, aldol condensation, ferrocenylenone, ultrasonic irradiation.

Aldol condensation reaction has long attracted the attention of chemical researchers[1-4]. Ferrocenylenones, as important intermediates in organic synthesis[5], are also obtainable by means of aldol condensation. They are uaually performed under classic homogeneous conditions in alcohol[6]; Toma *et al*. and collaborators described the synthesis of such products under phase-transfer conditions using 18-crown-6 ether as catalyst[7]. Recently, Villemin *et al*. reported that the synthesis of ferrocenylenones under microwave irradiation using Aliquat 336 which was generally efficient in liquid-solid phase-transfer catalysis (PTC)[8]. In the presence of KF-Al_2O_3 as a basic solid catalyst, acetylferrocene condensations with aromatic aldehydes gave α, β-unsaturated ketone substituted ferrocene derivatives in methanol for 6 hours[9].

A survey of literature shows that many organic reactions have recently been accelerated by ultrasonic irradiation[10-13]. Since the reaction time gets reduced and yields get improved under ultrasound irradiation condition, we decided to study the

Scheme



1-10 a) KOH / EtOH, rt., Ultrasonication **11-20**

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Table 1 The reaction of aromatic aldehydes with acetylferrocene in the presence of potassium hydroxide under ultrasonication at room temperature

Compd.	Ar-CHO	Products	Yield(%)[a]	mp. (°C)	
				Obtained	Reported[8,14]
1	*p*-$OCH_3C_6H_5$	**11**	92	153-154	153-154
2	*p*-$CH_3C_6H_5$	**12**	83	173-174	
3	C_6H_5	**13**	83	137-138	139-140
4	*P*-ClC_6H_5	**14**	82	161-162	160-161
5	*p*-$O_2NC_6H_5$	**15**	92	192	
6	*0*-ClC_6H_5	**16**	89	104-105	
7	3,4-$CH_2O_2C_6H_3$	**17**	76	167-168	169-170
8	C_4H_3S	**18**	83	146-147	145-147
9	C_4H_3O	**19**	88	155-156	155-157
10	C_5H_4N	**20**	90	152-153	152-153

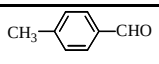
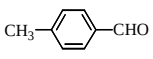
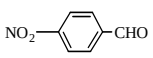
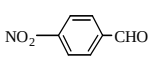
[a] Isolated yields.

possibility of the preparation of ferrocenyleones using Claisen-Schmidt condensation of different aromatic aldehydes with acetylferrocene under ultrasonication. Herein we report a facile synthesis of ferrocenylenone accelerated by ultrasonic irradiation, as shown in **Scheme**. All the results of the experiments are summarized in **Table 1**.

As can be seen from **Table 1**, it was found that the ultrasonic irradiation was very simple and convenient for the synthesis of ferrocenylenones (**11**-**20**) at room temperature using ultrasonic cleaner with a frequency of 40 kHz and a nominal power 100 W. In the experiment, the ultrasound technique represented a better procedure in terms of higher yield, milder reaction conditions, easier workup. For example, product **11** and product **13** were previously prepared in yield 53% and 63% respectively under microwave irradiation[8]. Whereas, under ultrasonication for 2 hours at room temperature in our operation, product **11** and product **13** were obtained in a 92% and 83% yield respectively.

It is worth noting that other bases can also be used in the reaction. The results are summarized in **Table 2**.

Table 2 Aldol condensation reaction under different basic conditions

Entry	Substrate	Additive	Yield(%)
1		NaOH	72
2		LiOH	77
3		NaOH	90
4		LiOH	89

From **Table 2**, we could easily find that NaOH and LiOH are also useful bases in aldol condensation reactions of acetylferrocene with aromatic aldehydes under the same conditions. Just as **Table 2** shows, with the participation of NaOH or LiOH, the reaction of p-tolualdehyde and p-nitrobenzaldehyde with acetylferrocene can also obtain high yields of product **12** (72%, 77%) (Entries 1, 2) and product **15** (90%, 89%) (Entries 3, 4) respectively.

General procedure: To an Ehrlenmeyer flask was charged with acetylferrocene (2.5 mmol), aromatic aldehyde (2.5 mmol), anhydrous ethanol (20 mL) and powdered potassium hydroxide (2.5 mmol) as base. The flask with the reaction mixture was immersed into the water bath of an ultrasonic cleaner at room temperature for 2 hours, and the reaction was monitored by TLC. At the end of the reaction, the ethanolic solution was evaporated on a rotatory evaporator *in vacuo* until the crystal appeared. 20 mL cold water was added to the former obtained solid mixture, stirred for a while, then neutralized with hydrochloric acid (10%). The product was collected by filtration and washed with cold water. The dry solid can be recrystallized from ethanol to give the purified product.

In conclusion, we have established a practical condensation procedure for the synthesis of ferrocenylenones under ultrasonic irradiation at room temperature. The operational simplicity, use of common and cheap additive (KOH), high yields and milder condition can make this procedure a useful and attractive alterative to the currently available methods.

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References

1. Z. W. Xie, Q. X. Fang, Y. L. Hu, M. X. Zhao, D. Yu, Q. Lin, *Chin. Chem. Lett.*, **1999**, *10* (1), 5.
2. M. S. Cheng, R. S. Li, G. Kenyon, *Chin. Chem. Lett.*, **2000**, *11* (10), 851.
3. X. Y. Chen, W. L. Bao, Y. M. Zhang, *Chin. Chem. Lett.*, **2000,** *11* (6), 483.
4. G. S. Deng, T. G. Ren, *Chin. Chem. Lett.*, **2001**, *12* (10), 859.
5. (a) O. Kocian, R. J. Mortimer, P. D. Beer, *J. Chem. Soc. Perkin Trans 1*, **1990**, 3203;
   (b) S. Kamiyama, A. Kasahara, T. Izumi, I. Shimizu, H. Watabe, *Bull. Chem. Soc. Jpn*., **1981**, *54*, 2079;
   (c) M. Hisatoma, J. Wastanabe, K. Yamakawa, K. Kozawa, T. Uchida, *Bull. Chem. Soc. Jpn*., **1995**, *68*, 635.
6. (a) K. Schlogl, *Monatsh. chem.*, **1957**, *88*, 601;
   (b) M. Furdik, P. Elecko, S. Toma, J. Suchy, *Chem. Zvesti*, **1960**, *15*, 501;
   (c) J. Biochard, J. P. Morin J. Triouflet, *Bull. Soc. Chim. Fr.*, **1963**, 851;
   (d) M. Rosenblum, *Chemistry of Iron Group Metalocenes*, parts I and II, Wiley, New York, **1965.**
7. M. Salisova, M. Puciova, U. N. Postnov S. Toma, *Chem. Papers*, **1990**, *44*, 201.
8. D. Villemin, B. Martin, M. Puciova, S. Toma, *J. Organometal. Chem.*, **1994**, *484*, 27.
9. C. Yan, B. Wang, J. Sun, W. Lu, *J. Yangzhou Uniu.*, **1999**, *2*, 22.
10. S. Yasui, A. Noguchi, Y. Yokoyama, *Jpn. kokai Tokkyo koho* Tp 04 36750, **1992**.
11. Z. Qin, F. Chem, Y. Xie, *Progr. Chem.*, **1998**, *10*, 298.
12. J. T. Li, L. J. Li, T. S. Li, J. Z. Wang, *Indian J. Chem.*, **1998**, *378*, 298.

13. J. T. Li, G. F. Chem, J. X. Wang, T. S. Li, *Synth. Commun.*, **1999**, *29*, 965.
14. K. Shibata, I. Katsuyama, M. Matsui, H. Muramatsu, *Bull. Chem. Soc. Jpn.*, **1990**, *63* (12), 3710.

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