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Note

Preparation of ferrocenyl mono- and dienone derivatives through aldol condensation of 1,1′-diacetylferrocene with aromatic aldehydes in dry conditions

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Abstract

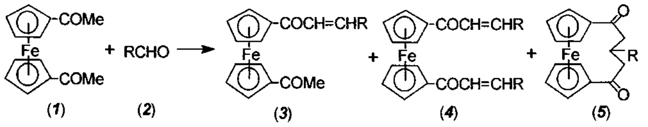
1,1′-Diacetylferrocene was condensed with aromatic aldehydes without solvent in the presence of solid NaOH. Diacetylferrocene can give good yields of mono- or diene with either one or two molecules of a wide range of aldehydes depending only on the stoichiometry. Cyclization to ferrocenphane does not occur in this condition.

Keywords: 1,1′-Diacetylferrocene; 1-Acetyl-1′-enonylferrocenes; 1,1′-Dienonylferrocenes; Aldol condensation; Solid-state reaction

1. Introduction

1,1′-Diacetylferrocenes are important compounds because of their photographic properties [1] and as precursors for semiconducting polymers [2]. Main synthetic methods for such ferrocenylenones are acylation [3] and aldol condensations [2,4]. However, the methods have serious disadvantages, such as use of large amounts of solvents, unavailable acyl chlorides [3], and low product yields [2,4]. Much attention has been focused on the Claisen–Schmidt reactions of 1,1′-diacetylferrocene with aromatic aldehydes in homogeneous solutions [5]. But, this reaction generally yields a mixture of 1,1′-dienonylferrocenes and ferrocenphane. In recent papers, the conditions to select the formation of the dienone derivative or the corresponding ferrocenphane have been established [6,7]. But they bear some of the following shortcomings: low yield, long reaction time, and reagent wasting. Recently, some aldol reactions of acetylferrocene in dry conditions with microwave irradiation for synthesis of ferrocenylenones were described [8]. The method has also some disavantages, such as needing PTC and combustion in the microwave oven. We have investigated the synthesis of ferrocenylenones using solid NaOH to catalyze this process under solvent-free conditions [9]. The main advantages of this procedure are the following: shorter reaction time, higher yields, and cleaner reaction with easier work-ups.

Herein, we report a selective synthesis of 1-acetyl-1′-enonylferrocenes (**3**) and 1,1′-dienonylferrocenes (**4**) without the ferrocenphane (**5**) by using a powdered NaOH catalyzed aldol condensation of diacetylferrocene with aromatic aldehydes (**2**) and a varying material ratio in a dry state. The operation has advantages, such as reduced pollution, low costs, high yields and simplicity in processing and handling.



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2. Results and discussion

The results are listed in Table 1 and in Section 3. All of the products were characterized by ^{1}H-NMR, MS and IR spectroscopy.

From Table 1, we can see that the aldol condensation can be carried out in mild conditions to give satisfactory yields of compounds **3** and **4**. When the ratio of **1**/**2** is 1:1, the principal product is **1** and the product **4** is also produced along with an increase of **2**. The **1** reacts completely when adding more aromatic aldehydes and the yields of **4** are also increased. From entry 7 to 16, we can infer that enones bearing electron-drawing groups on the aromatic ring are more reactive than those with electron-donating groups.

For reaction in presence of solvent, the condensation of diacetylferrocene and benzaldehyde with 5% aqueous–ethanolic sodium hydroxide produces a red product **4** and a yellow product **5** as it is shown in Table 2, and **5** is the principal product. By increasing the ratio of aldehyde, the amount of **4** was also increased and it became the principal product. However, under dry conditions, this condensation reaction gave **3** and another red product **4**. The red product **3** decreased and **4** increased as the molecular ratio of benzaldehyde was increased. Ferrocenyl mono- and dienone derivatives produced in this way have the *E*-configuration.

3. Experimental

3.1. Preparation of the materials

^{1}H-NMR spectra were performed on a DRX-200 spectrometer or a FC-80 spectrometer by using $CDCl_3$

Table 1
Preparation of compounds **3** and **4**

Entry	Ratio (ketone/aldehyde)	R	Time (min)	Temp. (°C)	Yield (%)		M.p. (lit) (°C)	
					Compd. **3**	Compd. **4**	Compd. **3**	Compd. **4**
1	1/1	Ph	20	40	68 (**3a**)	23 (**4a**)	131–132	181–183 (180–182) [4a]
2	1/3	Ph	20	40	Trace	92	(131–132) [4c]	181–183
3	1/1	2-Furyl	15	40	74 (**3b**)	12 (**4b**)	110–112	
4	1/3	2-Furyl	15	40	Trace	87		160 (162) [2]
5	1/1	PhCH=CH–	15	40	70 (**3c**)	15 (**4c**)	170–172	64–65
6	1/3	PhCH=CH–	15	40	Trace	94		
7	1/1	4-Cl–C_6H_4	20	70	56 (**3d**)	18 (**4d**)	160–161	216
8	1/2.5	4-Cl–C_6H_4	20	70	20	70		
9	1/1	3,4-$OCH_2OC_6H_3$	50	75	54 (**3e**)	10 (**4e**)	180	130–132
10	1/2.5	3,4-$OCH_2OC_6H_3$	50	75	8	69		
11	1/1	3-O_2N–C_6H_4	40	70	65 (**3f**)	10 (**4f**)	201–203 (200–202) [4b]	114–116
12	1/2.5	3-O_2N–C_6H_4	30	70	10	73		
13	1/1	4-$O_2NC_6H_3$	40	70	62 (**3g**)	12 (**4g**)	265 (265) [4b]	210
14	1/2.5	4-$O_2NC_6H_3$	40	70	11	75		
15	1/1	*p*-$N(CH_3)_2C_6H_4$	50	75	66 (**3h**)	8 (**4h**)	30–31	224
16	1/2.5		50	75	10	64		

Table 2
Aldol condensation reaction of **1** and **2a** in the dry state and in 5% NaOH aqueous EtOH [4a] with various equivalents of benzaldehyde

C_6H_5CHO equi.	Reaction temp. (°C)	Reaction time (min)	Solvent	Red product yield (%)		Yellow product yield (%)
				3a	**4a**	**5a**
1:1	r.t.	30	–	60–65	Trace	–
	15	90	EtOH [4a]	–	6–13	66–68
1:2	r.t.	30	–	40–45	20–22	–
	r.t.	90	EtOH [4a]	–	23	60
	40	240	MeOH [4b]	–	–	68
1:4	r.t.	25	–	–	96	–
	r.t.	90	EtOH [4a]	–	72	22
1:6	r.t.	360	EtOH [4a]	–	75	5

as a solvent and Me_4Si as an internal reference. Mass spectra were obtained on a ZAB-HS mass spectrometer by fast atom bombardment (FAB, MASPEC 11 date base). IR spectra were recorded on a Nicolet AVATAR 360 FT-IR spectrophotometer as KBr discs in the 4000–200 cm^{-1} region. The elemental analysis was carried out with an Elementary Vario EL analyzer. The melting points reported here were uncorrected. Diacetylferrocene (**1**) was synthesized as reported [10]. Aromatic aldehydes were purchased and used as received.

3.2. General procedure for the preparation of **3** and **4**

A mixture of **1** (1 mmol), **2** (1 mmol) and 0.2 g NaOH (5mmol) were ground with an agate mortar and a pestle, and allowed to stand at 40 °C (entry 1–6) or 70–75 °C (entry 7–16) for a specific time as shown in Table 1. The final products were extracted with CH_2Cl_2 and the solution was dried with $MgSO_4$. After filtration, the solvent was removed and the enones were separated from the residue by column chromatography (silica gel CH_2Cl_2–50% EtOAc as eluant).

3.2.1. *1-Acetyl-1′-cinnamoylferrocene* (**3a**)

Red solid, m.p. 131–132 °C. ^{1}H-NMR (δ, ppm): 7.87, 7.02 (dd, 2H, vinyl protons, $J = 15.5$ Hz), 7.9–7.2 (m, 5H, ph), 4.81, 4.79, 4.59, 4.52 (4t, 8H, Cp), 2.34 (s, 3H, CH_3); MS m/z (%): 358.2 (60), Anal. Calc. for $C_{21}H_{18}O_2Fe$: 358.2; IR (KBr, cm^{-1}): 1744 (C=O), 1668 (C=O), 1645 (C=C).

3.2.2. *1,1′-Dicinnamoylferrocene* (**4a**)

Red solid, m.p. 181–183 °C. ^{1}H-NMR (δ, ppm): 7.41, 7.02 (dd, 4H, vinyl protons, $J = 15.3$ Hz), 7.8–7.2 (m, 10H, ph), 4.93, 4.62, 4.26 (3m, 8H, Cp); MS *m*/*z* (%): 446.3 (90), Anal. Calc. for $C_{28}H_{22}O_2Fe$; 446.3; IR, (KBr, cm^{-1}): 1654 (C=O), 1572 (C=C).

3.2.3. *1-Acetyl-1′-(2-furyl)acryloylferrocene* (**3b**)

Red solid, m.p. 110–112 °C. ^{1}H-NMR (δ, ppm): 7.43 (s, 1H, furyl), 6.65 (s, 1H, furyl), 6.45 (s, 1H, furyl), 7.57, 6.93 (dd, 2H, vinyl, $J = 15.8$ Hz), 4.91, 4.79, 4.57, 4.54 (4t, 8H, Cp), 2.36 (s, 3H, CH_3); MS *m*/*z* (%): 347.2 (33), Anal. Calc. for $C_{19}H_{15}O_3Fe$: C, 65.75;H, 4.32. Found: C, 66.23; H, 4.81 IR (KBr, cm^{-1}): 1748 (C=O), 1667 (C=C), 1630 (C=C)..

3.2.4. *1,1′-bis[β-(2-Furyl)acryloyl]ferrocene* (**4b**)

Red solid. m.p. 160 °C. ^{1}H-NMR (δ, ppm): 7.46 (s, 2H, furyl), 6.67 (s, 2H, furyl), 6.48 (s, 2H, furyl), 7.56, 6.92 (dd, 4H, vinyl, $J = 15.2$ Hz), 4.93, 4,57 (2m, 8H, Cp); MS *m*/*z* (%): 426.2 (64), Anal. Calc. for $C_{24}H_{18}O_4Fe$:426.2; IR (KBr, cm^{-1}): 1650 (C=O), 1590 (C=C).

3.2.5. *1-Acetyl-1′-(β-phenylvinyl) acryloylferrocene* (**3c**)

Red solid, m.p. 170–172 °C. ^{1}H-NMR (δ, ppm): 7.85–7.24 (m, 5H, ph), 7.93, 7.04 (dd, 2H, $J = 15.1$ Hz, –C–CH = CH–), 6.74–6.54 (dd, 2H, $J = 15.2$Hz, –CH = CH–ph). 4.88, 4.59 (2m, 8H, Cp); MS *m*/*z* (%): 384.2 (50); Anal. Calc. for $C_{23}H_{20}O_2Fe$: C, 71.92; H, 5.21. Found: C, 71.45; H, 4.85%. IR(KBr, cm^{-1}) 1750 (C=O), 1670 (C=O), 1640 (C=C).

3.2.6. *1-1′-bis(β-Phenylvinyl)acryloylferrocene* (**4c**)

Red solid, m.p. 64–65 °C.^{1}H-NMR (δ, ppm): 7.90, 7.19 (dd, 4H, $J = 15.2$ Hz, –CCH = CH–), 6.99, 6.44 (dd, 4H, $J = 15.2$ Hz, –CH=CHph), 7.70–7.43 (m, 10H, ph), 4.96, 4.63 (2m, 8H, Cp); MS *m*/*z* (%): 498.3 (10), Anal. Calc. for $C_{32}H_{26}O_2Fe$: C, 77.13; H, 5.22. Found: C, 77.62; H, 5.69%. IR (KBr, cm^{-1}): 1658 (C=O), 1598 (C=C).

3.2.7. *1-Acetyl-1′-(p-chlorocinnamoyl)ferrocene* (**3d**)

Red solid, m.p. 160–161 °C. ^{1}H-NMR (δ, ppm): 7.89, 7.14 (dd, 2H, vinyl, $J = 15$ Hz), 7.70–7.48 (m, 4H, ph), 4.92, 4.80, 4.63, 4.55 (4t, 8H, Cp), 2.38 (s, 3H, CH_3); MS *m*/*z* (%): 392.7 (41), Anal. Calc. for $C_{21}H_{17}ClO_2Fe$: C, 64.22; H, 4.33. Found: C, 64.67; H, 4.68%. IR(KBr, cm^{-1}):1730 (C=O), 1665 (C=O), 1630 (C=C).

3.2.8. *1,1′-bis[(p-Chlorocinnamoyl)]ferrocene* (**4d**)

Red solid, m.p. 216 °C. ^{1}H-NMR (δ, ppm): 7.92, 7.04 (dd, vinyl, 4H, $J = 14.3$ Hz), 7.78–7.58 (m, 8H, ph), 4.95, 4.80, 4.67, 4.56 (4t, 8H, Cp); MS *m*/*z* (%): 515.3 (3), Anal. Calc. for $C_{28}H_{20}Cl_2O_2Fe$: C, 65.26; H, 3.88; Found: C, 65.67, H, 3.68%. IR (KBr, cm^{-1}): 1659 (C=O), 1588 (C=C).

3.2.9. *1-Acetyl-1′-piperonyloylferrocene* (**3e**)

Red solid, m.p. 180 °C. ^{1}H-NMR (δ, ppm): 7.64, 7.03 (dd, 2H vinyl, $J = 14.4$ Hz), 7.46–6.83 (m, 3H, ph), 6.50 (s, 2H, OCH_2O), 4.93, 4.52 (2m, 8H, Cp), 2.36 (s, 3H, CH_3); MS *m*/*z* (%) 402.3 (30), Anal. Calc. for $C_{22}H_{18}O_4Fe$: C, 68.66; H, 4.97; Found: C, 69.13; H, 4.57%. IR (KBr, cm^{-1}): 1740 (C=O), 1666 (C=O), 1635 (C=C).

3.2.10. *1,1′–bis-Piperonyloylferrocene* (**4e**)

Red solid, m.p. 130–132 °C. ^{1}H-NMR (δ, ppm): 7.79, 7.28 (dd, 4H, $J = 14.3$ Hz), 7.60–6.82 (m, 6H, ph), 6.01 (br, 4H, OCH_2O), 4.89, 4.60 (2m, 8H,Cp); MS *m*/*z* (%): 534.2(1.3), Anal. Calc. for $C_{30}H_{22}FeO_6$: C, 67.45; H, 4.12. Found: C, 67.48; H, 4.61%. IR (KBr, cm^{-1}): 1654 (C=O), 1593 (C=C).

3.2.11. *1-Acetyl-1′-(m-nitrocinnamoyl)ferrocene* (**3f**).

Red solid, m.p.. 201–201 °C. ^{1}H-NMR (δ, ppm): 8.22, 7.08 (dd, 2H, $J = 15$ Hz), 7.80–7.55 (m,4H, ph), 4.96, 4.90, 4.69, 4.62 (4t, 8H, Cp), 2.54 (s, 3H, CH_3);

MS *m*/*z* (%): 403.2(10), Anal. Calc. for $C_{21}H_{17}O_4NFe$: C, 62.55; H, 4.22; N, 3.47. Found: C, 62.98; H, 4.67; N, 3.78%. IR (KBr, cm^{-1}): 1720 (C=O), 1678 (C=O), 1600 (C=C).

3.2.12. *1,1′-bis(m-Nitrocinnamoyl)ferrocene (**4f**)*

Red solid, m.p. 108–109 °C, ^{1}H-NMR (δ, ppm): 8.26, 7.26, (dd, 4H, $J = 15$ Hz), 7.77–7.56 (m, 8H, ph), 4.94, 4.87, 4.65, 4.61 (4t, 8H, Cp); MS *m*/*z* (%): 536.7 (10), Anal. Calc. for $C_{28}H_{20}N_2O_6Fe$: C,62.65; H, 3.73; N, 5.38. Found: C, 62.89; H, 4.02; N, 4.98%. IR (KBr, cm^{-1}) 1658 (C=O), 1597 (C=C).

3.2.13. *1-Acetyl-1′-(p-nitrocinnamoyl)ferrocene (**3g**)*

Red solid, m.p. 265 °C, ^{1}H-NMR (δ, ppm): 8.37, 7.12 (dd, 2H, $J = 15$ Hz), 7.92–7.68 (m, 4H, ph), 4.97, 4.85, 4.68, 4.62 (4t, 8H, Cp), 2.60 (s, 3H, CH_3); MS *m*/*z* (%): 403.2 (15), Anal. Calc. for $C_{21}H_{17}O_4NFe$: C, 62.55; H, 4.22; N, 3.47. Found: C, 62.90; H, 4.71; N, 3.25%. IR (KBr, cm^{-1}): 1720 (C=O), 1640 (C=O), 1612 (C=C).

3.2.14. *1,1′-bis(p-Nitrocinnamoyl)ferrocene (**4g**)*

Red solid, m.p. 210 °C, ^{1}H-NMR (δ, ppm): 8.49, 7.26 (2dd, 4H, $J = 15.1$ Hz), 8.27–7.71 (m, 8H, ph), 4.98, 4.86, 4.68, 4.63 (4t, 8H, Cp); MS *m*/*z* (%): 536.7 (1), Anal. Calc. for $C_{28}H_{20}N_2O_6Fe$: C, 62.65; H, 3.73; N,5.38. Found: C, 62.18; H, 4.04; N, 4.96%. IR (KBr, cm^{-1}): 1660 (C=O), 1600 (C=C).

3.2.15. *1-Acetyl-1′-(p-N,N-dimethylcinnamoyl)ferrocene (**3h**)*

Red solid, m.p. 30–31 °C ^{1}H-NMR (δ, ppm): 7.68, 6.71 (dd, 2H, vinyl, $J = 15.6$ Hz), 7.48, 6.63 (m, 4H, ph), 4.89, 4.61, 4.30 (2m, 8H, Cp), 2.97 (s, 6H, $N(CH_3)_2$), 2.44 (s, 3H, CH_3); MS *m*/*z* (%): 401.2 (15), Anal. Calc. for $C_{23}H_{23}O_2NFe$: C, 68.85; H, 5.73; N, 3.49. Found: C, 69.15; H, 5.34; N, 3.87%. IR (KBr, cm^{-1}): 1730 (C=O), 1660 (C=O), 1630 (C=C).

3.2.16. *1,1′-bis-(p-N,N-Dimethylcinnamoyl)ferrocene (**4h**)*

Red solid, m.p. 224 °C ^{1}H-NMR (δ, ppm): 7.80, 6.90 (dd, 4H, vinyl, $J = 15.8$ Hz), 7.71–6.68 (m, 8H, ph), 4.95, 4.77, 4.55, 4.23 (4t, 8H, Cp), 2.98 (br, 12H, $N(CH_3)_2$); MS *m*/*z* (%): 533.4 (3), Anal. Calc. for $C_{32}H_{33}N_2O_2Fe$: C, 72.05; H, 6.19; N, 5.25. Found: C, 72.47; H, 6.63; N, 5.73%. IR (KBr, cm^{-1}): 1658 (C=O), 1572 (C=C).

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