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Journal of Organometallic Chemistry 637–639 (2001) 719–722

Journal of Organometallic Chemistry

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Note

Preparation of 1,5-diketone derivatives containing ferrocenyl by Michael reaction under solvent-free condition

Wan-yi Liu [a], Qi-hai Xu [a], Yong-min Liang [a], Bao-hua Chen [a], Wei-min Liu [b], Yong-xiang Ma [a,*]

[a] *National Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, People's Republic of China*
[b] *Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, People's Republic of China*

Received 12 November 2000; received in revised form 20 February 2001; accepted 21 February 2001

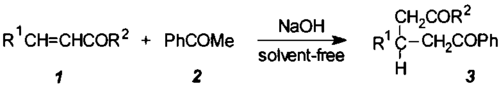
Abstract

This work describes a fast, mild, convenient and simple method for preparing 1,5-diketones by Michael reaction under solvent-free condition. Fourteen new 1,5-diketone compounds containing ferrocenyl were synthesized. The product **1f** is discussed from its ^{1}H-NMR spectrum. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Ferrocene; Ketone; Michael reaction; Solid-state reaction; Solvent-free

1. Introduction

1,5-Diketones are extremely important synthetic intermediates in their own right and are desirable starting materials for preparing many heterocyclic [1–3] and polyfunctional compounds [4–7]. These compounds, such as α,α-oligopyridines [4], terpyridylferrocene and bis(terpyridinylferrocene) [5] have potential applications in coordination chemistry, molecular sensing, catalytic reactions, the chemical modification of electrodes, and redox active self-assembly devices. According to the reports in literatures, there are four procedures for synthesizing 1,5-diketones: (i) by the aldol–Michael addition strategy [1,2,4,6]; (ii) the addition of activated methylene compounds to α,β-unsaturated ketones [3]; (iii) the condensation of ketone enolate and the Mannich base derived from methyl ketones [7]; and (iv) the conjugate addition of the enones to trimethylsilylenol ethers as donor [8]. These methods can be used for suitable reactive substrates, but there are some limitations, such as the reaction between aldehyde and acetophenone is only performed in alkaline alcohols and under refluxing condition. The aldehyde should have a drawing-electronic group and needs a large amount of solvent. In addition, these methods need to use more expensive reagents and have longer synthetic routes. The fourth method is considered to be a better one, but it should be carried under moisture- and oxygen-free conditions.



Scheme 1.

The solid-state Michael addition has been performed well recently [9–11]. However, until now this addition to ferrocene derivatives containing α,β-unsaturated ketones has attracted rather little attention [12–14], the addition of chalcone using acetophenone as Michael donor under solvent-free condition has not been reported so far. Herein, we describe this kind of reactions. It is shown that the 1,5-diketones containing ferrocenyl can be obtained in satisfactory yields by Michael addition in the dry state. The reaction has a

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* Corresponding author. Fax: + 86-931-8611688.
E-mail address: mayx@lzu.edu.cn (Y.-x. Ma).

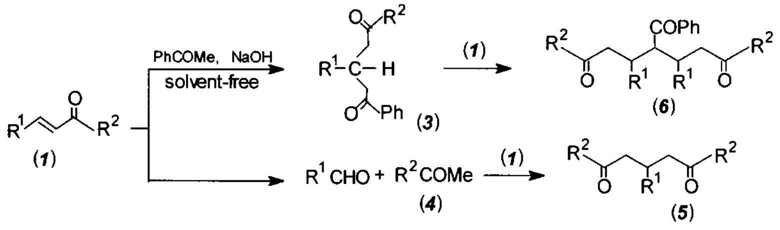
PII: S0022-328X(01)00894-4

Table 1
Preparation of compounds **3**

Entry	Compound	R^1	R^2	Time (h)	Yield (%) [a]	M.p. (°C)
1	**3a**	Ph	Fc	1.5	76.2	105–106
2	**3b**	3,4-OCH_2O–C_6H_3	Fc	1.5	79	143.5–144
3	**3c**	4-Me_2N–C_6H_4	Fc	1.5	68	140–141
4	**3d**	4-Cl–C_6H_4	Fc	1	87	137.5–138
5	**3e**	3-O_2N–C_6H_4	Fc	1 [b]	84	140–142
6	**3f**	PhCH=CH	Fc	1.5	71	129.5–130
7	**3g**	2-Furyl	Fc	1	73	93.5–94.5
8	**3h**	4-Fc–C_6H_4	Ph	1	82	141–142
9	**3i**	Fc	Fc	1.5	92	119–122

[a] Isolated yields.

[b] Carried out at room temperature.



Scheme 2.

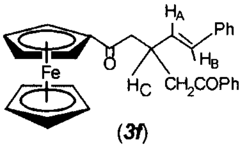
series of advantages, such as reduced pollution, low cost, mild conditions and simplicity in process and handling.

2. Result and discussion

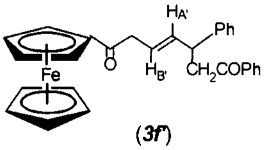
We prepared a series of ferrocenyl-1,5-diketones (**3**) through the Michael addition between a ferrocenylchalcone, $R^1CH{=}CHCOR^2$ (**1**), and benzophenone (**2**), using NaOH as catalyst in solvent-free and under mild conditions as shown in Scheme 1. The results are listed in Table 1.

It is known that the 1,5-dioxo-3,5-diphenylpentyl ferrocene (**3a**) is the only reported compound of this series [8]. It was prepared by conjugate addition to enones by enolates derived from base-induced cleavage of the O–Si bond of trimethylsily enol ether under argon atmosphere. That is, **2a** with enol silane (1.2 equivalents) in CH_2Cl_2 with degassed 5% aq. NaOH and 10 mol% tetrabutylammonium bromide as PTC. It can be seen that the operation is very tedious and the reagents are more expensive than those in our process.

From Table 1, we can see that Michael addition can be performed easily and gives product **3** in satisfactory yield. Compound **1** could react completely when we added a large amount of acetopenone (fivefold) and the yields of **3** increased and its reaction speed became fast. From entries 2–5, we might infer that enones bearing an electron-drawing group on the aromatic ring are more reactive than those with an electron-pushing group. The preparation of **3e** was performed at room temperature, but on heating the mixture soon turned black and no Michael adduct was obtained. Theoretically, entry 6 should have two Michael adducts, i.e. one of 1,4-addition (**3f**) and the other of 1,6-addition (**3f′**). But from the ^{1}H-NMR spectra, we can infer that **3f** is the only product of Michael addition. The chemical shift of H_A is 6.263–6.381 ppm as a double-doublet and that of H_B is 6.447–6.526 ppm as a doublet. If **3f′** is produced, the peak shape of $H_{A'}$ should be a double-doublet and that of $H_{B'}$ should be a double-triplet.



(3f)



(3f′)

We had also carried out the reaction of **1a** in different conditions, and we can see that higher temperature and longer reaction time may cut down the yield of the target product due to formation of some byproducts. Some of the byproducts have been isolated and characterized. So we can infer **1a** can decompose to acetylferrocene (**4**) and benzaldehyde. Compounds **4** and **1** also undergo Michael addition to form another 1,5-diketone (**5**) under reaction conditions. Compound **1** and product **3** react to form a triketone. That is, **1** can undergo reaction in solvent-free condition as shown in Scheme 2.

In summary, the Michael reaction of acetophenone with ferrocene-containing chalcones under solvent-free condition is a fast, mild and simple method to prepare ferrocenyl-1,5-diketone derivatives.

3. Experimental

^{1}H-NMR spectra were recorded on a DRX-200 spectrometer, except that of **3a**, **5b**, **3d**, **3i** and **5i**, which were recorded on a FC-80 spectrometer, using $CDCl_3$ as solvent and TMS as an internal standard. Mass spectra were obtained on a ZAB-HS mass spectrometer by fast atom bombardment (FAB, MASPEC II database). IR spectra were recorded in KBr on a Nicolet 1795X FTIR spectrophotometer. The elemental analysis was carried out with an Elementary Vario EL analyzer. The melting points reported are uncorrected.

3.1. Preparation of the materials

All compounds of **1** were synthesized as reported [15]. Acetophenone is commercially available and used directly.

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

A mixture of **1** (1 mmol), **2** (4 mmol) and 0.2 g NaOH (5 mmol) was ground with an agate mortar and a pestle, and allowed to stand at 45 °C for a specific time as shown in Table 1. (Note: entry 5 reacted at room temperature.) The final products were extracted with CH_2Cl_2 and the solution dried with $MgSO_4$. After filtration, the solvent was removed and the diketones were separated from the residue by column chromatography (silica gel, petroleum ether–5% EtOAc as eluant).

3a: 1,5-Dioxo-3,5-diphenylpentyl ferrocene. Orange–yellow needles, m.p. 105–106 °C. ^{1}H-NMR (δ, ppm): 3.13–3.22 (d, 2H, $FcCOCH_2$, $J = 6.7$ Hz); 3.40–3.52 (dd, 2H, $PhCOCH_2$, $^3J = 6.6$ Hz, $^2J = 3.4$ Hz); 3.92–4.19 (m, 1H, –CH); 4.07 (s, 5H, Cp-ring); 4.49 (s, 2H, Cp-ring); 4.78 (s, 2H, Cp-ring); 7.25–7.54 (m, 8H, Ph and PhCO); 7.93–8.04 (dd, 2H, PhCO, $J_o = 7.7$ Hz, $J_m = 2.1$ Hz). MS; m/z (%): 436.4 (33). IR (KBr, cm^{-1}): ν(C=O) 1657, 1683. Anal. Found: C, 72.97; H, 4.96. Calc. for $C_{27}H_{24}FeO_2$: C, 74.32; H, 5.54%.

3b: 1,5-Dioxo-3-(3,4-methylenedioxyphenyl)-5-phenylpentyl ferrocene. Orange–red solid, m.p. 143.5–144 °C. ^{1}H-NMR (δ, ppm): 3.08–3.11 (d, 2H, $FcCOCH_2$, $J = 7.0$ Hz); 3.23–3.52 (dd, 2H, $PhCOCH_2$, $^3J = 7.0$ Hz, $^2J = 16.2$ Hz); 3.89–4.05 (m, 1H, –CH); 4.07 (s, 5H, Cp-ring); 4.48 (s, 2H, Cp-ring); 4.77 (s, 2H, Cp-ring); 5.89 (s, 2H, O–CH_2–O); 6.70–6.84 (m, 3H, Ar); 7.41–7.56 (m, 3H, PhCO); 7.94–7.98 (d, 2H, PhCO, $J = 7.0$ Hz). MS; m/z (%): 480.1 (23). IR (KBr, cm^{-1}): ν(C=O) 1658, 1688. Anal. Found: C, 69.73; H, 4.73. Calc. for $C_{28}H_{24}FeO_4$: C, 70.01; H, 5.04%.

3c: 1,5-Dioxo-3-(4-*N*,*N*-dimethylaminophenyl)-5-phenylpentyl ferrocene. Yellow solid, m.p. 140–141 °C. ^{1}H-NMR (δ, ppm): 2.89 (s, 6H, NMe_2); 3.09–3.13 (d, 2H, $FcCOCH_2$, $J = 7.0$ Hz); 3.25–3.54 (dq, 2H, $PhCOCH_2$, $^3J = 7.2$ Hz, $^2J = 23.2$ Hz); 3.90–4.03 (m, 1H, –CH); 4.08 (s, 5H, Cp-ring); 4.47 (s, 2H, Cp-ring); 4.77 (s, 2H, Cp-ring); 6.67–6.72 (d, 2H, Ar, $J = 8.7$ Hz); 7.19–7.23 (d, 2H, Ar, $J = 8.7$ Hz); 7.40–7.58 (m, 3H, PhCO); 7.95–7.99 (d, 2H, PhCO, $J = 8.4$Hz). MS; m/z (%): 479 (73). IR (KBr, cm^{-1}): ν(C=O) 1670. Anal. Found: C, 72.55; H, 5.71; N, 2.92. Calc. for $C_{29}H_{29}FeNO_2$: C, 72.66; H, 6.10; N, 2.92%.

3d: 1,5-Dioxo-3-(4-choloro phenyl)-5-phenylpentyl ferrocene. Orange–red solid, m.p. 137.5–138 °C. ^{1}H-NMR (δ, ppm): 3.11–3.19 (d, 2H, $FcCOCH_2$, $J = 6.7$ Hz); 3.36–3.50 (m, 2H, $PhCOCH_2$); 3.85–3.98 (m, 1H, –CH); 4.11 (s, 5H, Cp-ring); 4.58 (s, 2H, Cp-ring); 4.79 (s, 2H, Cp-ring); 7.30 (s, 4H, Ar); 7.46–7.60 (br, 3H, PhCO); 7.92–8.02 (d, 2H, PhCO, $J = 7.1$ Hz). MS; m/z (%): 473 (27), 470.3 (61). IR (KBr, cm^{-1}): ν(C=O) 1658, 1688. Anal. Found: C, 68.43; H, 4.65. Calc. for $C_{27}H_{23}ClFeO_2$: C, 68.88; H, 4.92%.

3e: 1,5-Dioxo-3-(3-nitro phenyl)-5-phenylpentyl ferrocene. Orange–red solid, m.p. 140–142 °C. ^{1}H-NMR (δ, ppm): 3.10–3.32 (dq, 2H, $FcCOCH_2$, $^3J = 7.2$ Hz, $^2J = 16.4$ Hz); 3.35–3.62 (dq, 2H, $PhCOCH_2$, $^3J = 7.4$ Hz, $^2J = 16.2$ Hz); 4.06 (s, 5H, Cp-ring); 4.10–4.283 (m, 1H, –CH); 4.50 (s, 2H, Cp-ring); 4.81 (s, 2H, Cp-ring); 7.42–7.74 (m, 7H, Ar and PhCO); 7.93–7.96 (d, 2H, PhCO, $J = 7.0$ Hz), MS; m/z (%): 481 (34). IR (KBr, cm^{-1}): $\nu(NO_2)$ 1350, 1528, ν(C=O) 1676. Anal. Found: C, 66.97; H, 4.56. Calc. for $C_{27}H_{23}FeNO_4$: C, 67.38; H, 4.82; N, 2.91%.

3f: 1,5-Dioxo-5-phenyl-3-(2-phenyl ethenyl)pentyl ferrocene. Red solid, m.p. 129.5–130 °C. ^{1}H-NMR (δ, ppm): 2.90–3.16 (dq, 2H, $FcCOCH_2$, $^3J = 6.6$ Hz, $^2J = 18.0$ Hz); 3.12–3.46 (dq, 2H, $PhCOCH_2$, $^3J = 6.8$ Hz, $^2J = 16.2$ Hz); 3.50–3.69 (m, 1H, –CH); 4.18 (s, 5H, Cp-ring); 4.50 (s, 2H, Cp-ring); 4.82 (s, 2H, Cp-ring); 6.26–6.38 (dd, 1H, $CH_A{=}CH_B{-}CH_C{<}$, $J_{AB} = 15.8$ Hz, $J_{BC} = 7.8$ Hz); 6.45–6.53 (d, 1H, PhCH=C, $J = 15.8$ Hz); 7.14–7.34 (m, 5H, Ph); 7.43–7.56 (m, 3H, PhCO); 7.99–8.03 (d, 2H, PhCO, $J = 7.5$ Hz). MS; m/z (%): 462.2 (100). IR (KBr, cm^{-1}): ν(C=C–H) 969, ν(C=O) 1666. Anal. Found: C, 74.84; H, 5.17. Calc. for $C_{29}H_{26}FeO_2$: C, 75.33; H, 5.67%.

3g: 1,5-Dioxo-3-(2-furyl)-5-phenylpentyl ferrocene. Yellow solid, m.p. 93.5–94.5 °C. ^{1}H-NMR (δ, ppm): 3.23–3.28 (dq, 2H, $FcCOCH_2$, $^3J = 6.6$ Hz, $^2J = 16.4$ Hz); 3.34–3.55 (dq, 2H, $PhCOCH_2$, $^3J = 6.8$ Hz, $^2J = 16.4$ Hz); 4.01–4.23 (m, 1H, –CH); 4.13 (s, 5H, Cp-ring); 4.49 (s, 2H, Cp-ring); 4.79 (s, 2H, Cp-ring); 6.13 (s, 1H, furyl); 6.26 (s, 1H, furyl); 7.30 (s, 1H, furyl); 7.26–7.56 (m, 3H, PhCO); 7.97–8.01 (d, 2H, PhCO,

$J = 7.6$ Hz). MS; *m*/*z* (%): 426.2 (100). IR (KBr, cm^{-1}): ν(C=O) 1667. Anal. Found: C, 69.73; H, 5.30. Calc. for $C_{25}H_{22}FeO_3$: C, 70.44; H, 5.20%.

3h: 1,5-Dioxo-1,5-diphenyl-3-(4-ferrocenyl phenyl) pentane. Yellow solid, m.p. 141–142 °C. ^{1}H-NMR (δ, ppm): 3.37–3.49 (dq, 2H, $PhCOCH_2$, $^3J = 6.8$ Hz, $^2J = 13.2$ Hz); 3.86–4.03 (m, 1H, –CH); 4.10 (s, 5H, Cp-ring); 4.58 (s, 2H, Cp-ring); 4.81 (s, 2H, Cp-ring); 7.17–7.74 (m, 10H, *p*-Fc–C_6H_4 and PhCO); 7.99–8.03 (d, 4H, PhCO, $J = 7.8$ Hz). MS; *m*/*z* (%): 512 (21). IR (KBr, cm^{-1}): ν(C=O) 1680. Anal. Found: C, 77.57; H, 5.17. Calc. for $C_{33}H_{28}FeO_2$: C, 77.35; H, 5.51%.

3i: 1,5-Dioxo-3-ferrocenyl-5-phenylpentyl ferrocene. Yellow solid, m.p. 119–122 °C. ^{1}H-NMR (δ, ppm): 3.10–3.18 (d, 2H, $FcCOCH_2$, $J = 6.0$ Hz); 3.40–3.54 (br, 2H, $PhCOCH_2$); 3.74–3.91 (m, 1H, –CH); 4.16 (s, 10H, Cp-ring); 4.51 (s, 4H, Cp-ring); 4.80 (s, 4H, Cp-ring); 7.49–7.57 (br, 3H, PhCO); 8.01–8.10 (d, 2H, PhCO, $J = 7.8$ Hz). MS; *m*/*z* (%): 544 (81). IR (KBr, cm^{-1}): ν(C=O) 1662, 1686. Anal. Found: C, 68.68; H, 4.94. Calc. for $C_{31}H_{28}Fe_2O_2$: C, 68.41; H, 5.18%.

5a: 1,5-Dioxo-1,5-diferrocenyl-3-phenyl pentane. Yellow solid, m.p. 158–160 °C; obtained from **3a** (entry 1, Table 1) as a byproduct in 3% yield. ^{1}H-NMR (δ, ppm): 3.14–3.18 (d, 4H, $FcCOCH_2$, $J = 7.0$ Hz); 3.81–4.11 (m, 1H, –CH); 4.05 (s, 10H, Cp-ring); 4.47 (s, 4H, Cp-ring); 4.77 (s, 4H, Cp-ring); 7.17–7.41 (m, 5H, Ph). MS; *m*/*z* (%): 544.3 (48). Anal. Found: C, 68.01; H, 4.84. Calc. for $C_{31}H_{28}Fe_2O_2$: C, 68.41; H, 5.19%.

6a: 1,7-Dioxo-4-benzoyl-1,7-diferrocenyl-3,5-diphenyl heptane. Yellowish solid, m.p. 180–183 °C; obtained from **3a** (entry 1, Table 1) as a byproduct in 9% yield. ^{1}H-NMR (δ, ppm): 2.96–3.39 (m, 4H, $2FcCOCH_2$); 3.71–4.73 (m, 21H, Cp-ring and –CH); 7.05–7.94 (m, 15H, Ar). MS; *m*/*z* (%): 752.2 (31). Anal. Found: C, 72.97; H, 4.96. Calc. for $C_{46}H_{40}Fe_2O_3$: C, 73.42; H, 5.36%.

5b: 1,5-Dioxo-1,5-diferrocenyl-3-(3,4-methyleneoxyphenyl) pentane. Orange–yellow solid, m.p. 167–169 °C; obtained from **3b** (entry 2, Table 1) as a byproduct in 5% yield. ^{1}H-NMR (δ, ppm): 3.08–3.16 (d, 4H, $FcCOCH_2$, $J = 6.8$ Hz); 3.80–4.09 (br, 1H, –CH); 4.12 (s, 10H, Cp-ring); 4.51 (s, 4H, Cp-ring); 4.80 (s, 4H, Cp-ring); 5.91 (s, 2H, O–CH_2–O); 6.87–6.93 (m, 3H, Ar). MS; *m*/*z* (%): 588.1 (69). Anal. Found: C, 64.92; H, 4.68. Calc. for $C_{32}H_{28}Fe_2O_4$: C, 65.34; H, 4.80%.

5i: 1,5-Dioxo-1,3,5-triferrocenyl pentane. Red solid, m.p. 183–185 °C; obtained from **3i** (entry 9, Table 1) as a byproduct in 5% yield. ^{1}H-NMR (δ, ppm): 3.15–3.22 (d, 4H, $FcCOCH_2$, $J = 5.6$ Hz); 3.76–3.98 (br, 1H, –CH); 4.19 (s, 15H, Cp-ring); 4.52 (s, 6H, Cp-ring); 4.85 (s, 6H, Cp-ring). MS; *m*/*z* (%): 652.2 (84). Anal. Found: C, 63.58; H, 4.47. Calc. for $C_{35}H_{32}Fe_3O_2$: C, 64.46; H, 4.95%.

6g: 1,7-Dioxo-4-benzoyl-1,7-diferrocenyl-3,5-di-(2-furyl) heptane. Yellow solid, m.p. 106–107 °C; obtained from **3g** (entry 7, Table 1) as a byproduct in 7% yield. ^{1}H-NMR (δ, ppm): 2.860–3.361 (m, 4H, $FcCOCH_2$); 3.77–4.71 (m, 21H, Cp-ring and –CH); 5.89–6.20 (m, 4H, furyl); 7.10 (s, 1H, furyl); 7.22 (s, 1H, furyl); 7.38–7.83 (m, 5H, Ph). MS; *m*/*z* (%): 732.5 (42); Anal. Found: C, 68.50; H, 4.57. Calc. for $C_{42}H_{36}Fe_2O_5$: C, 68.87; H, 4.95%.

References

[1] Z.S. Arigan, H. Suschitiky, J. Chem. Soc. (1961) 2242.
[2] S.S. Hirsch, W.J. Bailey, J. Org. Chem. 43 (1978) 4091.
[3] F. Krohnke, Synthesis (1976) 1.
[4] E.C. Constable, A.M.W. Cargill Thompson, J. Chem. Soc. Dalton Trans. (1992) 2947.
[5] K.T. Potts, Bull. Soc. Chem. Belg. 99 (1990) 741.
[6] I.R. Butler, S.J. Mcdonald, Polyhedron 14 (1995) 529.
[7] N.S. Gill, K.B. James, F. Lions, K.T. Potts, J. Am. Chem. Soc. 74 (1952) 4923.
[8] V.M. Swamy, A. Sarka, Tetrahdron Lett. 39 (1998) 1261.
[9] B.S. Goud, K. Panneerselvam, D.E. Zacharias, G.R. Desiraju, J. Chem. Soc. Perkin Trans. 2 (1995) 325.
[10] S. Annunziata, S. Aldo, R.D. Margherita, G. Manueia, S. Arrigo, Tetrahedron Lett. 38 (1997) 289.
[11] X.L. Li, Y.M. Wang, T. Matsuura, J.B. Meng, J. Heterocyc. Chem. 36 (1999) 697.
[12] J. Tirouflet, J. Boichardt, Bull. Soc. Chim. Fr. (1963) 851.
[13] J. Federic, S. Toma, Collect. Czech. Chem. Commun. 52 (1987) 174.
[14] Z.X. Bian, Y.G. Liu, F.Z. Li, Huaxue Shiji 16 (1994) 175.
[15] W.Y. Liu, Q.H. Xu, Y.X. Ma, Syn. Commun. in press.