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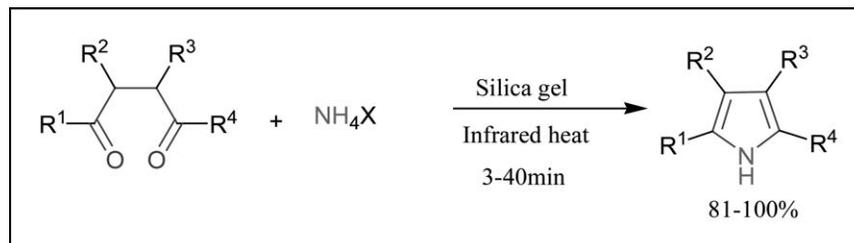
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Received July 29, 2010

DOI 10.1002/jhet.744

Published online 13 September 2011 in Wiley Online Library (wileyonlinelibrary.com).



A facile amination of 1,4-diketones with ammonium acetate has been achieved by mechanochemical grinding assisted by infrared irradiation in the presence of silica gel. The wastes are reduced and the energy resources saved.

J. Heterocyclic Chem., **49**, 204 (2012).

INTRODUCTION

The pyrrole unit is one of the most abundant heterocycles in natural products [1] and medicinal agents [2]. As versatile building blocks, pyrroles have been widely used in heterocyclic chemistry [3] and materials science [4]. Hitherto, a great many of methods have been developed for the synthesis of these five-membered heterocycles [5], including classical Knorr reaction [6], Hantzsch reaction [7], Paal-Knorr condensation reaction [8] and other new strategies [9]. However, upon these well-established procedure, some drawbacks still exists, for instance, high temperatures [10], long reaction times [11,8a], low yields [12] and complicated workup procedures [13].

With growing interest in better methodologies for the preparation of pyrroles, it is quite necessary to explore facile, green and practical methods. In recent years, organic chemists have paid much attention to solvent-free reactions [14] owing to the easy isolation and purification of the products as well as the low environment pollution. Based on our previous work, a well-established method for synthesis of β -enamino ketones from 1,3-diketones at solid state [15], we turned our interest to preparation of pyrroles.

In this article, we report that an infrared aided synthesis of pyrroles was accomplished using inorganic ammonium salts as a nitrogen source and silica gel as a catalyst.

RESULTS AND DISCUSSION

Initially, a model reaction was established just by grinding a mixture of 1,4-diketone and ammonium acetate under radiation of infrared lamp for appropriate

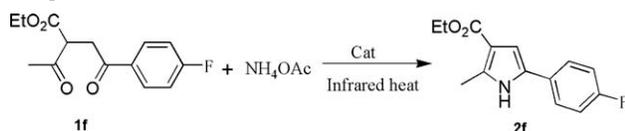
time. Various catalysts were investigated and the results were summarized in Table 1.

Generally used catalysts such as triflates, KHSO₄, sulfuric acid, *p*-toluenesulfonic acid and formic acid were firstly employed in our model reaction. However, poor to moderate yields were given (Table 1, entries 1–7). According to our previous work [15], we chose silica gel as a catalyst to explore the solid state organic reactions. To our surprise, as a weak Lewis acid, silica gel showed high activity in the reactions. The best result was obtained in the case of 20 mol % silica gel employed as a catalyst, and the conversion of diketone was proceed smoothly in 96% yield (Table 1, entry 9). the dosage of silica gel, whether increasing or decreasing, did not improve the reaction noticeably (Table 1, entries 10, 11). As expected, the blank reaction without addition of any catalyst gives low yield (Table 1, entry 8). Furthermore, silica gel was easy to be recovered and reused with only a little loss of its activity (Table 1, entry 12). Though good yield was given by conventional way of refluxing in acetic acid, it takes long reaction time. Above all, silica gel catalyzed grinding synthesis of pyrroles from 1,4-diketones and ammonium salts, assisted by infrared irradiation, were superior to other reaction systems known, because of the advantage of excellent yield, short reaction time and no metal pollution.

Under the similar conditions, a variety of ammonium salts were screened, and the corresponding results were listed in Table 2. As illustrated, ammonium salt of weak acids such as NH₄HCO₃, NH₄OAc, (NH₄)₂CO₃, and NH₄OOCH exhibited good activity because of their easy release of NH₃ during the reactions. In contrast, when ammonium salt of strong acids, such as NH₄Cl, (NH₄)₂SO₄, were used, the low yields were given.

Table 1

Condensation of 1,4-diketone **1f** with ammonium acetate in the presence of various acids under different reaction conditions.^a



Entry	Catalyst	Time (min)	Yield ^b (%)
1	Sm(OTf) ₃	40	82
2	Mn(OTf) ₃	35	68
3	Pr(OTf) ₃	38	84
4	KHSO ₄	30	76
5	HCOOH ^c	35	43
6	H ₂ SO ₄ ^d	30	67
7	<i>p</i> -TsOH	30	89
8	Neat	40	48
9	Silica gel ^e	20	96
10	Silica gel ^f	35	84
11	Silica gel ^g	20	95
12	Silica gel ^h	25	91
13	Silica gel ⁱ	80	32
14	CH ₃ COOH ^j	180	92

^aGeneral process: grinding reactants with catalyst together for 1 minute then allowed to stand under infrared lamp for appropriate times.

^bIsolated products.

^c10% mol HCOOH as catalyst.

^d5% mol H₂SO₄ as catalyst.

^e20 mol % catalyst was used.

^f10 mol % catalyst was used.

^g30 mol % catalyst was used.

^hThe catalyst was reused after heated at 120°C for half an hour.

ⁱGrinding reactants with catalyst together at room temperature.

^jCH₃COOH and CH₃OH as solvent at reflux temperature.

To evaluate the scope and limitations of this solid state reaction system, different substituted 1,4-diketones were tested, from which functionalized pyrroles were synthesized under the optimized reaction conditions (Table 3). As shown in Table 3, this system is suitable for both symmetrical 1,4-diketones (Table 3, entries 1,2) and unsymmetrical ones (Table 3, entries 3–11).

It is noticed that pyrroles can be synthesized smoothly from ammonium acetate and 1,4-diketones (Table 3, entries 1–11) except diphenyl diketone **1m** (Table 3, entry 12). And it seems like that the electron withdrawing substituents in R² and R³ position of **1** promote the reaction (Table 3, compare entries 3, 4 with entries 10, 11), and the aryl groups in R¹ and R⁴ positions deactivate the reactions.

As a contrast, the reactions were carried out in 70°C heat oven (Table 3, yields in the parentheses) instead of under infrared heat. It is observed that infrared heat facilitates promoting amination process. The experimental results show that infrared heat can reach or be superior to the yield of conventional heating procedure, but the reaction time is greatly reduced which also improves the efficiency of the experiment.

CONCLUSION

In summary, we have developed an efficient and solvent-free Paal-Knorr synthesis of pyrroles under mild conditions. This simple catalytic method represents an attractive pathway to synthesis of pyrroles. Compared with the traditional method, there are at least four advantages: (1) the way of energy supply (infrared heat) is harmless; (2) the reaction was carried out in solid state which means that no volatile organic compounds (VOCs) was used in this method; (3) the reaction time is short (in most cases less than 30 minutes); (4) It avoids the usage of any metal compound and corrosive acid which may cause the pollution. The only catalyst used in this reaction is silica gel, which can be easily recycled.

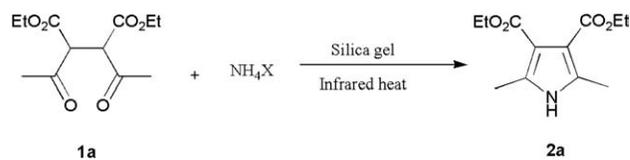
EXPERIMENTAL

Melting points were determined on a Büchi B-540 melting apparatus and are uncorrected. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker Model Avance III 500 MHz spectrometer in CDCl₃ or DMSO-*d*₆, using TMS as the internal standard and chemical shifts are given in δ relative to the solvent peak. Mass spectra were measured with Agilent 6210 TOF LC/MS (APCI, ESI) mass spectrometer. TLC was performed on silica gel GF 254. Infrared lamp was used with 250 W and the silica gel was 200–300 mesh heated under 120°C for half an hour.

General procedure for the preparation of pyrroles from 1,4-diketones and ammonium salts. A mixture of 1,4-diketones (1.0 mmol), ammonium acetate (116 mg, 1.5 mmol) and 20 mol % silica gel (13 mg) was grinded in mortar at room temperature for 1 minute. Then let it under infrared lamp for several minutes. After completion of the reaction as indicated by TLC, the reaction mixture was extracted with CH₂Cl₂ twice

Table 2

The result of solid state reactions of 1,4-diketone **1a** with different ammonium salts.^a



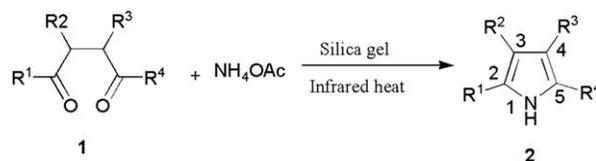
Entry	Ammonium salt	Time (min) ^b	2	Yield (%) ^c
1	NH ₄ HCO ₃	7	2a	98
2	NH ₄ OAc	3	2a	100
3	(NH ₄) ₂ CO ₃	13	2a	97
4	NH ₄ OOCH	5	2a	99
5	NH ₄ Cl	40	2a	41
6	(NH ₄) ₂ SO ₄	40	2a	26

^aGeneral process: grinding reactants with amount of silica gel together for 1 minute then allowed to stand under infrared lamp for appropriate times.

^bThe time is the best reaction time.

^cIsolated yields.

Table 3

The result of different 1,4-diketones with ammonium acetate.^a

Entry	1, 1,4-Diketone R ¹ , R ² , R ³ , and R ⁴	Time/min ^b	2	Yield ^c (%)
1	1a , R ¹ =R ⁴ =CH ₃ , R ² =R ³ =CO ₂ Et	3 (25)	2a	100 (98)
2	1b , R ¹ =R ⁴ =CH ₃ , R ² =R ³ =CO ₂ Me	13 (60)	2b	97 (92)
3	1c , R ¹ =CH ₃ , R ² =CO ₂ Me, R ³ =H, R ⁴ =Ph	24 (75)	2c	96 (94)
4	1d , R ¹ =CH ₃ , R ² =CO ₂ Et, R ³ =H, R ⁴ =Ph	30 (105)	2d	91 (87)
5	1e , R ¹ =CH ₃ , R ² =CO ₂ Me, R ³ =H, R ⁴ =4-FC ₆ H ₄	16 (80)	2e	97 (98) ^d
6	1f , R ¹ =CH ₃ , R ² =CO ₂ Et, R ³ =H, R ⁴ =4-FC ₆ H ₄	20 (120)	2f	96 (97) ^d
7	1g , R ¹ =CH ₃ , R ² =CO ₂ Me, R ³ =H, R ⁴ =4-OHC ₆ H ₄	13 (70)	2g	96 (98)
8	1h , R ¹ =CH ₃ , R ² =Ac, R ³ =H, R ⁴ =Ph	12 (65)	2h	94 (91)
9	1i , R ¹ =CH ₃ , R ² =Ac, R ³ =H, R ⁴ =4-FC ₆ H ₄	20 (70)	2i	89 (87) ^d
10	1j , R ¹ =Ph, R ² =R ³ =H, R ⁴ =CH ₃	14 (50)	2j	81 (79)
11	1k , R ¹ =CH ₃ , R ² =COPh, R ³ =H, R ⁴ =Ph	40 (130)	2k	83 (76)
12	1m R ¹ =R ⁴ =Ph, R ² =R ³ =H	60	/	Trace

^aGeneral process: 1,4-diketones (1mmol), ammonium acetate (1.5 mmol) and silica gel (20 mol %) under infrared heat (the temperature detected was below 70°C), yields are given for isolated products.

^bThe data showed in the parentheses were performed at 70°C in common oven.

^cYields are given for isolated products.

^d1,4-Diketones (1 mmol), ammonium salts (2.5 mmol).

(2 × 8 mL). The combined organic layers were dried over MgSO₄, concentrated under reduced pressure to give a product with high purity. The solid product could be further purified by recrystallization in CH₂Cl₂.

2,5-Dimethyl-1H-pyrrole-3,4-dicarboxylic acid diethyl ester (2a). Yield: 100%; mp 85–86°C; ref. [16a] 96–98°C; ¹H NMR (500 MHz, CDCl₃): δ = 1.32 (t, *J* = 7.0 Hz, 6H), 2.35 (s, 6H), 4.24–4.29 (q, *J* = 7.0, 14.5 Hz, 4H), 8.30 (s, 1H). ¹³C NMR (500 MHz, CDCl₃): δ = 12.17, 14.25, 60.02, 112.24, 132.47, 165.74.

2,5-Dimethyl-1H-pyrrole-3,4-dicarboxylic acid dimethyl ester (2b). Yield: 97%; mp 114–115°C; ref. [16b] 115–117°C; ¹H NMR (500 MHz, CDCl₃): δ = 2.36 (s, 6H), 3.81 (s, 6H), 8.37 (s, 1H). ¹³C NMR (500 MHz, CDCl₃): δ = 12.37, 51.27, 112.27, 132.54, 165.89.

2-Methyl-5-phenyl-1H-pyrrole-3-carboxylic acid methyl ester (2c). Yield: 96%; mp 138–139°C; ¹H NMR (500 MHz, CDCl₃): δ = 2.59 (s, 3H), 3.83 (s, 3H), 6.82 (d, *J* = 3.0 Hz, 1H), 7.21–7.24 (m, 1H), 7.34–7.37 (m, 2H), 7.44–7.46 (m, 2H), 8.53 (s, 1H). ¹³C NMR (500 MHz, CDCl₃): δ = 13.28, 50.85, 107.34, 113.07, 123.71, 126.57, 128.91, 130.12, 131.85, 136.34, 166.04.

2-Methyl-5-phenyl-1H-pyrrole-3-carboxylic acid ethyl ester (2d). Yield: 91%; mp 108–110°C; ref. [16c] 112–113°C; ¹H NMR (500 MHz, CDCl₃): δ = 1.36 (t, *J* = 7.5 Hz, 3H), 2.59 (s, 3H), 4.28–4.32 (q, *J* = 7.0 Hz, 2H), 6.84 (d, *J* = 3.0 Hz, 1H), 7.21–7.24 (m, 1H), 7.35–7.38 (m, 2H), 7.44–7.46 (m, 2H), 8.47 (s, 1H). ¹³C NMR (500 MHz, CDCl₃): δ = 13.34, 14.51, 59.52, 107.39, 113.41, 123.71, 126.52, 128.89, 130.03, 131.90, 136.20, 165.66.

5-(4-fluorophenyl)-2-methyl-1H-pyrrole-3-carboxylic acid methyl ester (2e). Yield: 97%; mp 178–180°C; ¹H NMR (500 MHz, CDCl₃): δ = 2.58 (s, 3H), 3.83 (s, 3H), 6.75 (d, *J* = 3.0

Hz, 1H), 7.04–7.08 (m, 2H), 7.39–7.42 (m, 2H), 8.48 (s, 1H). ¹³C NMR (500 MHz, CDCl₃): δ = 13.32, 50.94, 107.17, 113.10, 115.84, 116.01, 125.38, 125.44, 128.15, 129.23, 136.28, 160.70, 162.66, 165.90. hrms (ESI) [M-H]⁻ m/z Calcd for C₁₃H₁₁FN O₂: 232.0774; Found: 232.0783.

5-(4-fluorophenyl)-2-methyl-1H-pyrrole-3-carboxylic acid ethyl ester (2f). Yield: 96%; mp 138–140°C; ¹H NMR (500 MHz, CDCl₃): δ = 1.36 (t, *J* = 7.0 Hz, 3H), 2.58 (s, 3H), 4.27–4.31 (q, 2H, *J* = 7.0 Hz), 6.76 (d, *J* = 3.0 Hz, 1H), 7.04–7.07 (m, 2H), 7.40–7.42 (m, 2H), 8.52 (s, 1H). ¹³C NMR (500 MHz, CDCl₃): δ = 13.29, 14.46, 59.63, 107.16, 113.23, 115.70, 115.87, 125.39, 125.46, 128.24, 128.25, 129.30, 136.34, 160.63, 162.59, 165.82.

5-(4-hydroxyphenyl)-2-methyl-1H-pyrrole-3-carboxylic acid methyl ester (2g). Yield: 96%; mp 167–168°C; ¹H NMR (500 MHz, DMSO-*d*₆): δ = 2.45 (s, 3H), 3.69 (s, 3H), 6.54 (d, *J* = 3.0 Hz, 1H), 6.74–6.77 (m, 2H), 6.41–6.44 (m, 2H), 9.41 (s, 1H), 11.41 (s, 1H). ¹³C NMR (500 MHz, DMSO-*d*₆): δ = 12.77, 50.39, 104.42, 111.33, 115.55, 123.24, 125.06, 130.16, 135.67, 156.03, 165.15. hrms (ESI) [M-H]⁻ m/z Calcd for C₁₃H₁₂N O₃: 230.0817; Found: 230.0824.

3-Acetyl-2-methyl-5-phenyl-1H-pyrrole (2h). Yield: 94%; mp 185–186°C; ref. [16d] 179–181°C; ¹H NMR (500 MHz, CDCl₃): δ = 2.46 (s, 3H), 2.62 (s, 3H), 6.78 (d, *J* = 3.0 Hz, 1H), 7.23–7.26 (m, 1H), 7.36–7.39 (m, 2H), 7.47–7.49 (m, 2H), 8.82 (s, 1H); ¹³C NMR (500 MHz, CDCl₃): δ = 14.09, 28.45, 107.45, 122.26, 123.78, 126.71, 128.97, 129.89, 131.73, 136.02, 195.23.

3-Acetyl-2-methyl-5-(4-fluorophenyl)-1H-pyrrole (2i). Yield: 89%; mp 232°C; ref. [16e] 220°C; ¹H NMR (500 MHz, CDCl₃): δ = 2.45 (s, 3H), 2.61 (s, 3H), 6.70 (d, *J* = 3.0 Hz, 1H), 7.07–7.10 (m, 2H), 7.41–7.44 (m, 2H), 8.43 (s, 1H). ¹³C NMR (500 MHz, DMSO-*d*₆): δ = 13.31, 14.04, 20.70,

28.31, 59.69, 107.26, 115.44, 115.62, 121.58, 125.29, 125.36, 128.32, 128.56, 128.58, 159.66, 161.59, 193.47.

2-Methyl-5-phenyl-1H-pyrrole (2j). Yield: 81%; mp 94–96°C; ref. [16f] 95°C; ¹H NMR (500 MHz, CDCl₃): δ = 2.34 (s, 3H), 5.95–5.96 (m, 1H), 6.40 (t, *J* = 3.0 Hz, 1H), 7.15–7.18 (m, 1H), 7.32–7.35 (m, 2H), 7.42–7.44 (m, 2H), 8.11 (s, 1H). ¹³C NMR (500 MHz, CDCl₃): δ = 13.19, 106.23, 107.97, 123.35, 125.66, 128.81, 129.03, 130.81, 133.00.

2-Methyl-3-benzoyl-5-phenyl-1H-pyrrole (2k). Yield: 83%; mp 200–203°C; ref. [16g] 205–206°C; ¹H NMR (500 MHz, CDCl₃): δ = 2.65 (s, 3H), 6.68 (d, *J* = 3.0 Hz, 1H), 7.22–7.26 (m, 1H), 7.36–7.39 (m, 2H), 7.45–7.48 (m, 4H), 7.52–7.55 (m, 1H), 7.83–7.85 (m, 2H), 8.60 (s, 1H). ¹³C NMR (500 MHz, CDCl₃): δ = 13.91, 109.19, 121.24, 123.80, 126.68, 128.10, 128.95, 129.02, 129.81, 131.25, 131.71, 137.59, 140.51, 192.53.

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