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Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information: http://www.tandfonline.com/loi/lsyc20

Ionic Liquid as Catalyst and Reaction Medium: A Simple and Efficient Procedure for Paal-Knorr Furan Synthesis

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To cite this article: Gangqiang Wang , Zhi Guan , Rongchang Tang & Yanhong He (2010): Ionic Liquid as Catalyst and Reaction Medium: A Simple and Efficient Procedure for Paal-Knorr Furan Synthesis, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 40:3, 370-377

To link to this article: <u>http://dx.doi.org/10.1080/00397910902978049</u>

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IONIC LIQUID AS CATALYST AND REACTION MEDIUM: A SIMPLE AND EFFICIENT PROCEDURE FOR PAAL-KNORR FURAN SYNTHESIS

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The ionic liquid 1-butyl-3-methyl-imidazolium hydrogen sulfate, $[bmim]HSO_4$, efficiently catalyzes Paal–Knorr furan synthesis without any organic solvent. A wide range of aliphatic and aromatic 1,4-diketones easily undergo condensations to form furan derivatives, providing a general and convenient procedure. The Paal–Knorr reaction of ester-substituted 1,4-diketones is first reported. The ionic liquid can be recovered and reused for subsequent runs without any appreciable loss of efficiency.

Keywords: Catalyst; furan derivatives; ionic liquid; Paal-Knorr reaction; reaction medium

The furan ring can be found in many pharmaceutical and natural products,^[1,2] and it is a useful building block in synthetic organic chemistry.^[3] Among the various methods of furan synthesis, the Paal-Knorr reaction is the most widely used approach, in which 1,4-dicarbonyl compounds are converted to furan derivatives via acidmediated dehydrative cyclization.^[4–6] In recent years, with the development of many excellent methods for the preparation of 1,4-diones,^[7-18] the synthetic utility of this century-old reaction has experienced rekindled interest. Generally, hazardous organic solvents, strong acids such as H₂SO₄, P₂O₅, and *p*-toluenesulfonic acid (p-TSA), have been employed for the Paal-Knorr furan synthesis,^[19-21] and long reaction times were often required for the condensation. These may not be the preferred choices in view of green chemistry. Hence, an efficient and environmentally benign Paal-Knorr condensation is needed for contemporary chemical synthesis. Ionic liquids have recently emerged as environmentally friendly alternatives for organic synthesis. Use of ionic liquids in organic synthesis, particularly those based on an imidazolium cation,^[22-26] have experienced an impetus. However, their use in Paal-Knorr furan synthesis remains largely unexplored. There is only one report by Yadav et al. about the usage of Bi(OTf)3 immobilized in [bmim]BF4 as a catalytic system for the Paal–Knorr furan synthesis.^[27] Therefore, we report the facile and

Received January 21, 2009.

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high-yielding Paal–Knorr reaction using [bmim]HSO₄ ionic liquid alone as an efficient and recyclable catalyst as well as a green reaction medium.

In the present method, dehydrative cyclization of 1,4-diketones in ionic liquid [bmim]HSO₄ at 150°C afforded furans in good to quantitative yields. To assess the generality of the method, aryl and alkyl, di-, tri-, and tetra-substituted 1,4-dicarbonyl compounds were transformed to the furan derivatives (Table 1). The method is efficient and easy to carry out. The reactions were complete within 2–5 h, and the products were easily isolated by simple extraction with diethyl ether. All the nonester-containing aromatic 1,4-diketones (2a and 4a-9a, entry 2 and entries 4-9) provided corresponding furan products in quantitative yields after simple extraction and removal of the solvents. However, alkyl-substituted 1,4-diketones (1a and 3a, entries 1 and 3) gave furan products in lesser yields (84% and 80% respectively). For 1,4-diketone hexane-2,5-dione (1a, entry 1), in consideration of the volatility, the reaction was first carried out at 60°C in ionic liquid, which furnished furan in only 21% yield with the starting material recovered after 24 h. From thin-layer chromatography (TLC) no side products were observed. Then, the reaction temperature was raised to 150° C in a sealed tube within an oven without stirring, which gave the product in 84% yield after 4h. From TLC, the reaction was clean and the starting material has been consumed, so the poor yield is probably due to the volatility of the product. In the case of 1-phenylpentane-1,4-dione (3a, entry 3), it provided the product furan in 80% yield. No starting material was remained, and some unidentified side products were observed.

Interestingly, when trisubstituted 1,4-diketo-2-esters (10a-18a, entries 10-18) were submitted to the cyclization, the corresponding furan esters were obtained, accompanied by decarboxylated furan products. We found that when C-1 was substituted by CH_3 or Ph, the furan esters were obtained as the major products (entries 10–15), but when C-1 was substituted by the strong electron-withdrawing group $(p-)NO_2Ph$, the decarboxylated furans were received as the major products (entries 16–18). It seems that the strong electron-withdrawing group on C-1 of diketones facilitates the decarboxylation of C-2 ester. However, no decarboxylation was observed for tetrasubstituted 1,4-diketo-2-esters (19a-21a, entries 19-21), which provided corresponding furan esters as the only products in quantitative yields, regardless of whether there was an electron-donating (CH_3) or electronwithdrawing [Ph or (p)NO₂Ph] group on C-1. When 1,4-dimethyl-2,3-diester butane-1,4-dione (22a, entry 22) was submitted to the cyclization reaction, the decarboxylated product monoester furan 22c was obtained in 53% yield as the only product without diester furan detected. The reaction was clean; the poor yield of **22c** probably due to its volatility. Nevertheless, the cyclization of 1,4-diphenyl-2,3diester butane-1,4-dione (23a) showed the contrasting results. The diester furan 23b was received as the major product, and the decarboxylated product monoester furan 23c was obtained as the minor one. It can be seen that the substituents can strongly influence the decarboxylation of ester-containing 1,4-diketones. The Paal-Knorr reaction of ester-substituted 1,4-diketones has not been reported, to our best knowledge.

A proposed mechanism for the conversion of 1,4-diketones into furans using ionic liquid is given in Scheme 1. The ionic liquid [bmim] HSO_4 provides protons as a Brønsted acid to catalyze the reaction. First, the protonation of one carbonyl

Entry	1,4-Diketone	Furan	Time (h)	Yield (%)
1	Me Me 1a	Me Me 1b	4	84 ^c
2		S S 2b	3	100 ^b
3	Ph Me 3a	PhMe 3b	2	80 ^c
4	Ph Ph 4a	Ph Ph Ab	2	100 ^b
5	(p)MePh O 5a	(p)MePh PhMe(p) 5b	2	100 ^b
6	(p)CIPh PhCI(p) 0 6a	(p)CIPh PhCI(p) 6b	2	100 ^b
7	$(p)BrPh \longrightarrow 0 PhBr(p) O Ta$	(p)BrPh PhBr(p) 7b	2	100 ^b
8	Ph Ph Ph 8a	Phy Ph Ph 8b	2	100 ^b
9	Ph He O 9a	Ph Ph Ph Me Me 9b	2	100 ^b
10	$Me \xrightarrow[EtO_2C]{Ph} 10a$	$\frac{\text{Me} + 0}{\text{EtO}_2 C} + \frac{\text{Ph}}{10b} = \frac{\text{Me} + 0}{10c} + \frac{\text{Ph}}{10c}$	3	10b : 60 ^c 10c : 28 ^c
11	Me PhNO ₂ (p) EtO ₂ C 0 11a	$\begin{array}{ccc} \text{Me} & & & \\ & & & \\ & & & \\ \text{EtO}_2\text{C} & & \\ & & & \\ \end{array} \begin{array}{ccc} \text{Me} & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ \end{array} \begin{array}{cccc} \text{Me} & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ \end{array} \begin{array}{ccccccccccccccccccccccccccccccccccc$	3	11b : 71 ^c 11c : 14 ^c
12	$Me \qquad PhNO_2(m) \\ FtO_2C \qquad 0 \qquad 12a$	$\begin{array}{ccc} Me & & & \\ & & & \\ & & & \\ EtO_2C & 12b & & 12c \end{array}$	3	12b: 80 ^c 12c: 7 ^c
13	Ph Ph Ph Ph Ph $13a$	$Ph \xrightarrow{O} Ph$ $Ph \xrightarrow{O} Ph$ EtO ₂ C 13b 13c	4	13b : 55 ^c 13c : 34 ^c
14	$\begin{array}{c} 0 \\ Ph \\ EtO_2C \end{array} \begin{array}{c} PhNO_2(p) \\ 14a \end{array}$	$\begin{array}{ccc} Ph & O & PhNO_2(p) \\ EtO_2C & 14b & 14c \end{array}$	4	14b : 71 ^{<i>c</i>} 14c : 14 ^{<i>c</i>}
15	Ph Ph FtO ₂ C Ph D	$\begin{array}{c} Ph & O \\ Ph & Ph NO_2(m) \\ EtO_2C \\ 15b \\ 15c \\ \end{array}$) 4	15b : 70 ^c 15c : 23 ^c

Table 1. Cyclization of 1,4-diketones into furans using ionic liquid at $150^{\circ}C^{a}$

(Continued)

Entry	1,4-Diketone	Furan	Time (h)	Yield (%)
16	$(p)O_2NPh$ Ph Ph EtO_2C O 16a	$(p)O_2NPh \xrightarrow{O} Ph \qquad (p)O_2NPh \xrightarrow{O} Ph$ $EtO_2C \qquad 16b \qquad 16c$	4	16b : 7 ^c 16c : 90 ^c
17	$(p)O_2NPh \qquad \qquad$	$(p)O_2NPh \xrightarrow{O} PhNO_2(p)$ $EtO_2C \xrightarrow{(p)O_2NPh} \xrightarrow{O} PhNO_2(p)$ $17b \xrightarrow{I7c}$	4	17b: 5 ^c 17c: 91 ^c
18	$(p)O_2NPh \underbrace{\downarrow}_{EtO_2C} PhNO_2(m) \\ 18a$	$(p)O_2NPh \downarrow^O PhNO_2(m)$ $EtO_2C (p)O_2NPh \downarrow^O PhNO_2(m)$ $18b 18c$) 4	18b : 10 ^c 18c : 85 ^c
19	Me Ph EtO ₂ C 0 19a	$\begin{array}{c} Me \\ \hline \\ EtO_2C \\ Me \end{array} \begin{array}{c} Ph \\ 19b \end{array}$	3	19b : 100 ^b
20	$\begin{array}{c} O & Me \\ Ph & Ph \\ EtO_2C & O \end{array} \begin{array}{c} Ph \\ 0 \\ 20a \end{array}$	Ph Ph EtO ₂ C Me 20b	4	20b : 100 ^b
21	$(p)O_2NPh \qquad \qquad Ph \\ EtO_2C \qquad O \qquad 21a$	(p)O ₂ NPh EtO ₂ C Me 21b	4	21b : 100 ^b
22	$Me \qquad Me \qquad Me \\ EtO_2C \qquad 22a$	Me Me CO ₂ Et 22c	5	22c : 53 ^c
23	$\begin{array}{c} O & CO_2Et \\ Ph & Ph \\ EtO_2C & O & 23a \end{array}$	$\begin{array}{c} Ph & Ph & Ph & O \\ EtO_2C & CO_2Et & 23b & CO_2Et \end{array} 23c \end{array}$	5	 23b: 63^c 23c: 14^c

Table 1. Continued

^aThe reaction was carried out in a sealed tube at 150°C within an oven without stirring.

^{*b*}Yield of crude product of >95% purity by NMR.

^cYield of isolated product after flash chromatography.

group generates protonated species, which undergoes enolization. Then, intramolecular nucleophilic attack of the enol oxygen upon the electrophilic carbon of another protonated carbonyl group takes place. The final step is the dehydration to furnish furan derivatives.

Finally, to verify that the ionic liquid could be reused, it was recovered from the cyclization of **7a**, washed with diethyl ether $(2 \times 10 \text{ mL})$ to remove any organic impurity and dried in vacuo for use in subsequent reactions.^[28,29] The reaction was performed three times using the same ionic liquid without any appreciable loss of efficiency.

In summary, we have developed a facile and efficient method for the most widely used Paal-Knorr furan synthesis. In comparison with reported protocols, the method presented herein avoids the use of metals, mineral acids, organic solvents, and other hazardous chemicals and instead employs ionic liquid



Scheme 1. Plausible mechanism for the Paal-Knorr furan synthesis catalyzed by [bmim]HSO₄ ionic liquid.

 $[bmim]HSO_4$ as an efficient and reusable catalyst as well as a green reaction medium, which is easy to separate from the product mixture by simple extraction. The reaction is high-yielding and easy to perform.

EXPERIMENTAL

Typical Procedure for the Synthesis of Substituted Furans

A solution of 1,4-dione **15a** (0.353 g, 0.7 mmol) in ionic liquid [bmim]H-SO₄(1.6 g, 6.7 mmol) was stirred at 150°C for 4 h in oil bath. After cooling to rt, the reaction mixture was thoroughly extracted with diethyl ether. The combined extracts were washed with water and brine, dried (Na₂SO₄), and filtered. The solvents were removed, and the residue was purified by flash chromatography (petroleum ether/dichloromethane 2:1) to get **15b** (240 mg, 70%) as yellow crystals and **15c** (43 mg, 23%) as yellow crystals.

Compound 15b. Mp: $130-131^{\circ}$ C ¹H NMR (300 MHz, CDCl₃): $\delta = 8.52-7.46$ (m, 9H), 7.24 (s, 1H), 4.34 (q, 2H, J = 7.1 Hz), 1.37 (t, 3H, J = 7.1 Hz); ¹³C NMR (75 MHz, CDCl₃): $\delta = 163.0$, 157.5, 149.6, 148.7, 131.3, 129.9, 129.8, 129.3, 129.1, 128.4, 128.2, 122.3, 118.6, 116.0, 110.2, 60.8, 14.2. HRMS (EI) calcd. for C₁₉H₁₅NO₅ 337.095; found 337.0953.

Compound 15c. Mp: 134–135°C; ¹H NMR (300 MHz, CDCl₃): $\delta = 8.52-7.31$ (m, 9H), 6.88 (s, 1H), 6.77 (s, 1H); ¹³C NMR (75 MHz, CDCl₃): $\delta = 154.7$, 150.7, 148.7, 132.2, 130.1, 129.7, 129.0, 128.8, 128.0, 123.9, 121.5, 118.2, 109.5, 107.4. HRMS (EI) calcd. for C₁₆H₁₁NO₃ 265.0739; found 265.0738.

Spectroscopic Data of Selected Compounds

Compound 12b. Yellow crystals. ¹H NMR (300 MHz, CDCl₃): $\delta = 8.47-7.53$ (m, 4H), 7.05 (s, 1H), 4.34 (q, 2H, J = 7.1 Hz), 2.68 (s, 3H), 1.38 (t, 3H, J = 7.1 Hz);

¹³C NMR (75 MHz, CDCl₃): $\delta = 163.5$, 159.8, 149.2, 148.8, 131.6, 129.8, 129.0, 122.0, 118.3, 115.9, 107.9, 60.4, 14.3, 13.9.

Compound 12c. Yellow crystals. Mp: 71–72°C; ¹H NMR (300 MHz, CDCl₃): $\delta = 8.43-7.47$ (m, 4H), 6.69 (s, 1H), 6.11 (s, 1H), 2.39 (s, 3H); ¹³C NMR (75 MHz, CDCl₃): $\delta = 153.5$, 149.8, 148.7, 132.6, 129.5, 128.6, 121.0, 117.9, 108.2, 13.7. HRMS (EI) calcd. for C₁₁H₉NO₃ 203.0582; found 203.0583.

Compound 14b. Yellow crystals. Mp: $174-175^{\circ}$ C; ¹H NMR (300 MHz, CDCl₃): $\delta = 8.30-7.48$ (m, 9H), 7.32 (s, 1H), 4.35 (q, 2H, J = 7.1 Hz), 1.37 (t, 3H, J = 7.1 Hz); ¹³C NMR (75 MHz, CDCl₃): $\delta = 162.9$, 158.2, 149.8, 146.8, 135.3, 130.0, 129.0, 128.5, 128.2, 124.4, 124.1, 116.3, 111.8, 60.9, 14.2. HRMS (EI) calcd. for C₁₉H₁₅NO₅ 337.095; found 337.0962.

Compound 16b. Yellow crystals. Mp: $128-129^{\circ}$ C; ¹H NMR (300 MHz, CDCl₃): $\delta = 8.32-7.32$ (m, 9H), 7.09 (s, 1H), 4.35 (q, 2H, J = 7.1 Hz), 1.39 (t, 3H, J = 7.1 Hz); ¹³C NMR (75 MHz, CDCl₃): $\delta = 162.9$, 153.7, 152.9, 147.3, 135.2 128.9, 128.8, 128.7, 128.4, 124.1, 123.3, 118.6, 108.5, 61.1, 14.2. HRMS (EI) calcd. for C₁₉H₁₅NO₅ 337.095; found 337.0953.

Compound 17b. Yellow crystals. Mp: 240–241°C ¹H NMR (300 MHz, CDCl₃): $\delta = 8.35-7.90$ (m, 8H), 7.38 (s, 1H), 4.38 (q, 2H, J = 7.1 Hz), 1.41 (t, 3H, J = 7.1 Hz); ¹³CNMR (75 MHz, CDCl₃): $\delta = 162.5$, 155.0, 151.4, 148.0, 147.4, 134.7, 129.1, 124.6, 123.6, 119.0, 112.1, 61.4, 14.2. HRMS (EI) calcd. for C₁₉H₁₄N₂O₇ 382.0801; found 382.0796.

Compound 18b. Yellow crystals. Mp: $177-178^{\circ}$ C; ¹H NMR (300 MHz, CDCl₃): $\delta = 8.55-7.63$ (m, 8H), 7.31 (s, 1H), 4.39 (q, 2H, J = 7.1 Hz), 1.42 (t, 3H, J = 7.1 Hz); ¹³CNMR (75 MHz, CDCl₃): $\delta = 162.5$, 154.3, 151.2, 148.8, 147.8, 134.8, 130.6, 130.1, 129.6, 123.5, 123.0, 118.9, 110.7, 61.4, 14.2. HRMS (EI) calcd. for C₁₉H₁₄N₂O₇ 382.0801; found 382.0802.

Compound 18c. Yellow crystals. Mp: $158-159^{\circ}$ C; ¹H NMR (300 MHz, CDCl₃): $\delta = 8.57-7.60$ (m, 8H), 6.98 (s, 1H), 6.97 (s, 1H); ¹³C NMR (75 MHz, CDCl₃): $\delta = 152.8$, 152.2, 148.8, 146.7, 135.6, 131.5, 130.0, 129.5, 124.4, 124.1, 122.5, 118.7, 111.3, 110.0. HRMS (EI) calcd. for C₁₆H₁₀N₂O₅ 310.0590; found 310.0593.

Compound 19b. White crystals. ¹H NMR (300 MHz, CDCl₃): $\delta = 7.58-7.29$ (m, 5H), 4.30 (q, 2H, J = 7.1 Hz), 2.60 (s, 3H), 2.39 (s, 3H), 1.36 (t, 3H, J = 7.1 Hz); ¹³C NMR (75 MHz, CDCl₃): δ 164.7, 158.3, 147.6, 130.9, 128.4, 127.1, 126.0, 116.8, 115.2, 59.8, 14.3, 10.8.

Compound 21b. ¹H NMR (300 MHz, CDCl₃): $\delta = 8.28-7.30$ (m, 9H), 4.12 (q, 2H, J = 7.1 Hz), 2.36 (s, 3H), 0.98 (t, 3H, J = 7.1 Hz); ¹³C NMR (75 MHz, CDCl₃): δ 164.3, 150.4, 147.0, 135.7, 132.2, 129.4, 128.1, 127.4, 123.9, 123.6, 117.8, 61.0, 13.5, 12.1. HRMS (EI) calcd. for C₂₀H₁₇NO₅ 351.1107; found 351.1105.

Compound 22c. ¹H NMR (300 MHz, CDCl₃): $\delta = 6.21$ (1H, s), 4.26 (2H, q, J = 7.1 Hz), 2.52 (3H, s), 2.36 (3H, s), 1.33 (3H, t, J = 7.1 Hz); ¹³C NMR (75 MHz, CDCl₃) $\delta = 164.4$, 157.6, 150.0, 114.2, 106.3, 60.0, 14.5, 13.7, 13.2.

ACKNOWLEDGMENTS

Financial support from the Scientific Research Foundation for the Returned Overseas Chinese Scholars of the State Education Ministry, the Natural Science Foundation Project of Chongqing, Chongqing Science & Technology Commission (CQ CSTC) (2006BB5377), the High-Tech Training Fund of Southwest University (XSGX0601), and the Doctoral Fund of Southwest University (SWNUB2005012) is gratefully acknowledged.

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