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Ionic liquid as catalyst and solvent: the remarkable effect of a basic ionic liquid, [bmIm]OH on Michael addition and alkylation of active methylene compounds

Brindaban C. Ranu,* Subhash Banerjee and Ranjan Jana

Department of Organic Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700 032, India

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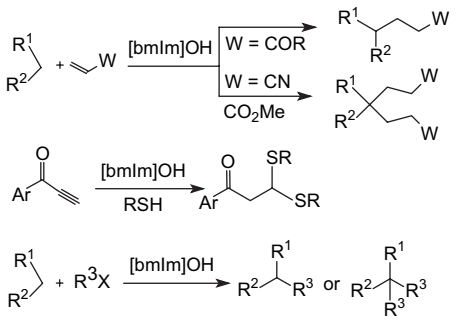
Abstract—A basic ionic liquid, 1-methyl-3-butylimidazolium hydroxide, [bmIm]OH, catalyzes the Michael addition of active methylene compounds to conjugated ketones, carboxylic esters and nitriles. It further catalyzes the addition of thiols to α,β-acetylenic ketones and alkylation of 1,3-dicarbonyl and -dicyano compounds. The Michael addition to α,β-unsaturated ketones proceeds in the usual way, giving the monoaddition products, whereas addition to α,β-unsaturated esters and nitriles leads exclusively to the bis-addition products. The α,β-acetylenic ketones undergo double conjugate addition with thiols producing β-keto 1,3-dithio-derivatives. In the alkylation reaction the acyclic 1,3-diketones are monoalkylated, whereas cyclic ketones undergo dialkylation under identical conditions. All these reactions were carried out without any organic solvent. The ionic liquid can also be recycled.

1. Introduction

Ionic liquids have been the subject of considerable interest in the context of green synthesis because of their wide acceptability as alternative green reaction media.[1] Recently, the ionic liquids have been found to act as catalysts for several reactions.[2] As a part of our continued efforts to design new task specific ionic liquids for chemical transformations,[3] we previously introduced a basic ionic liquid, 1-methyl-3-butylimidazolium hydroxide [bmIm]OH, as an efficient catalyst for Michael addition.[4] This ionic liquid showed a remarkable influence on the reaction by directing the addition of conjugated esters and nitriles to 1,3-dicarbonyl compounds to give bis-adducts.[4] This interesting observation prompted us to explore the potential of this ionic liquid for other related reactions. In the meantime another group[5] used our ionic liquid for Markovnikov addition of *N*-heterocycles to vinyl esters. Very recently, we disclosed the efficiency of [bmIm]OH for catalyzing Knoevenagel condensation.[6] Here its application in the Michael addition of thiols to α,β-acetylenic ketones and alkylation of 1,3-dicarbonyl compounds, together with the detailed and additional results of Michael additions disclosed in our preliminary communication[4] are reported (Scheme 1).



Scheme 1.

2. Results and discussion

The experimental procedures for all these reactions are straightforward. For carbon–carbon bond formation (Michael addition), a mixture of active methylene compound (malononitrile, entry 21, Table 1) and conjugated alkene (methyl acrylate, entry 21, Table 1) was stirred at room temperature without any organic solvent in the presence of [bmIm]OH. In the case of C–S Michael addition [bmIm]OH was diluted with another neutral ionic liquid, [bmIm]Br, to

Keywords: Michael addition; Alkylation; Ionic liquid; Catalysis; Microwave.
* Corresponding author. Tel.: +91 33 24734971; fax: +91 33 24732805; e-mail: ocbcr@iacs.res.in

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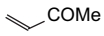
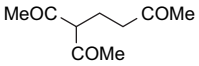
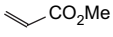
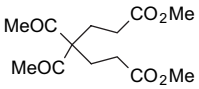
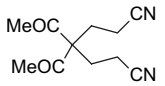
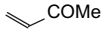
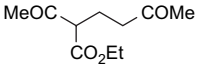
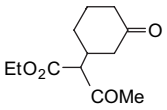
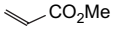
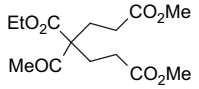
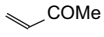
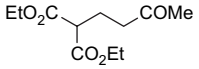
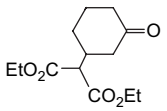
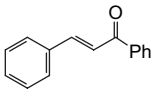
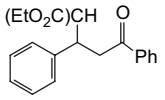
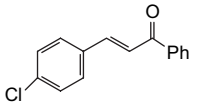
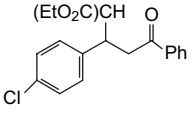
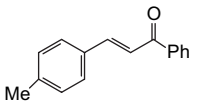
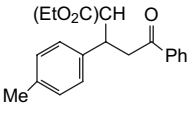
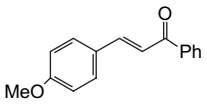
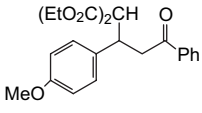
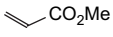
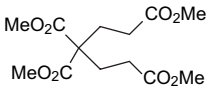
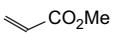
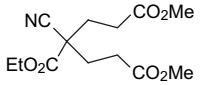
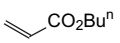
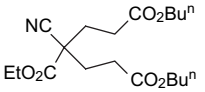
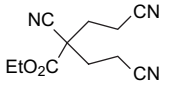
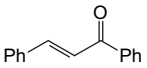
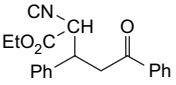
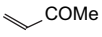
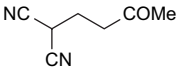
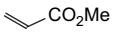
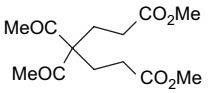
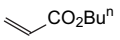
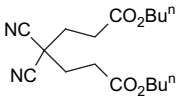
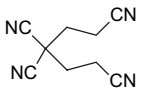
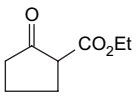
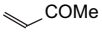
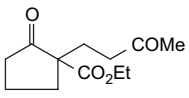
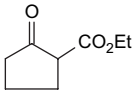
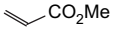
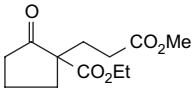
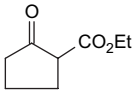
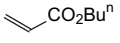
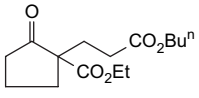
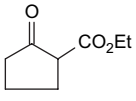
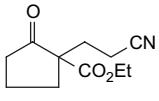
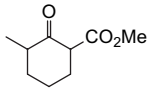
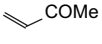
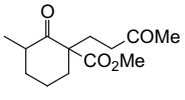
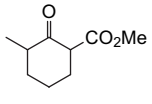
Table 1. Michael addition catalyzed by [bmIm]OH

Entry	Michael donor	Michael acceptor	Product	Time (h)	Yield[a] (%)	Ref.
1				0.5	95	4
2				2.0	95	4
3				2.0	85	4
4				0.75	90	4
5				3.5	90	4
6				2.5	95	4
7				1.5	95	4
8				4.0	90	4
9				2.5	95	4
10				3.0	90	4
11				3.0	90	4
12				3.0	85	4
13				2.5	85	4
14				3.0	82	4
15				0.5	96	4

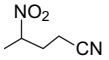
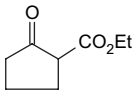
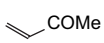
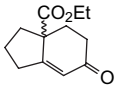
(*continued*)

Table 1. (*continued*)

Entry	Michael donor	Michael acceptor	Product	Time (h)	Yield[a] (%)	Ref.
16				2.5	92	4
17				2.0	90	—
18				2.5	92	4
19				2.5	92	4
20				0.5	95	7
21				1.5	95	7
22				2.0	92	—
23				1.0	96	—
24				0.5	96	4
25				2.0	90	4
26				2.5	85	—
27				2.0	92	4
28				1.0	90	4
29				2.0	92	4
30	$CH_3CH_2NO_2$			0.5	90	4
31	$CH_3CH_2NO_2$			3.0	90	4

(*continued*)

Table 1. (*continued*)

Entry	Michael donor	Michael acceptor	Product	Time (h)	Yield[a] (%)	Ref.
32	$CH_3CH_2NO_2$			3.0	90	4
33				2.5[b]	80	4

[a] Yields refer to those of pure isolated products characterized by IR, ^{1}H and ^{13}C NMR spectroscopic data.
[b] The reaction was carried out at 110 °C.

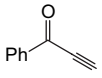
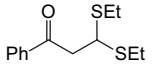
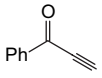
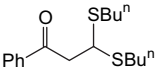
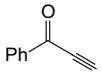
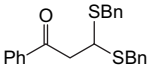
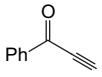
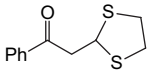
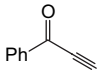
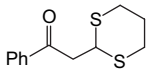
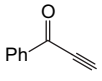
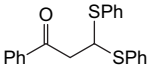
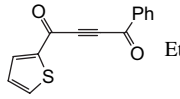
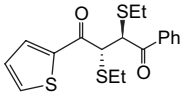
get the best results. For alkylation of active methylene compounds the reactions were carried out under microwave irradiation. In general, the products were isolated by direct distillation. However, when the reaction was carried out in small scale (less than 1 mmol) the product was isolated by extraction with ethyl acetate.

A wide range of structurally diverse active methylene compounds underwent Michael additions with several conjugated alkenes such as α,β-unsaturated ketones, carboxylic esters and nitriles affording the corresponding products in high yields (Table 1). Very interestingly, acetyl acetone, ethyl acetoacetate, diethyl malonate, ethyl cyanoacetate and malononitrile reacted with conjugated ketones such as methyl vinyl ketone, cyclohexenone and chalcones to produce the usual monoaddition products (entries 1, 4, 5, 7–12, 15, 19 and 20), whereas the same substrates behaved differently with acrylic esters and acrylonitrile (entries 2, 3, 6, 13, 14, 16–18 and 21–23) giving bis-addition products. The use of 0.5 equiv or less of methyl acrylate or acrylonitrile in these reactions did not produce any monoaddition product; only the bis-addition products were isolated in proportionate yields. On the other hand, the use of excess methyl vinyl ketone did not furnish the bis-addition product under identical reaction conditions. However, very surprisingly, the reaction of nitroethane with methyl vinyl ketone, methyl acrylate and acrylonitrile proceeded in the usual way giving monoaddition products (entries 30–32). In Michael addition, although monoadduct was obtained with all conventional acidic and basic reagents,[7] the formation of bis-adducts in one step with methyl acrylate and acrylonitrile is not unprecedented; reported to be possible using a ruthenium(II) complex.[7j] However, the disadvantages of this specific procedure are long reaction times (48–96 h) and relatively low yields (60–89%). Nevertheless, the great significance of this rather unusual bis-addition is the formation of two C–C bonds in one step; moreover, these adducts have some synthetic potential, as they contain several important functional groups. The cyclic β-keto esters also underwent facile additions by this procedure (entries 24–29). However, the reaction of cyclopentanone carboxylate (entry 33) with methyl vinyl ketone at 110 °C furnished the annulated bicyclic conjugated ketone by a tandem reaction of Michael addition followed by aldol condensation.

Several thiols and dithiols underwent double conjugate addition with conjugated terminal acetylenic ketones in the presence of this ionic liquid, [bmIm]OH, to produce the corresponding β-keto 1,3-dithane derivatives. These compounds are of much importance in organic synthesis.[8] The results are reported in Table 2. The internal acetylenic diketone provided *trans*-vicinal dithia-derivatives (entry 7) as indicated by the coupling constants (J=11.6 Hz) in ^{1}H NMR spectra, using this procedure.

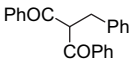
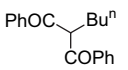
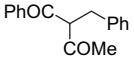
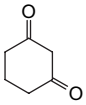
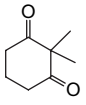
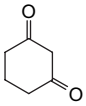
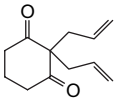
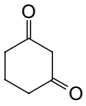
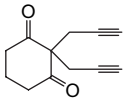
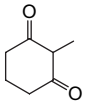
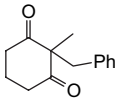
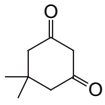
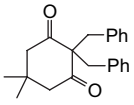
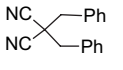
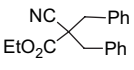
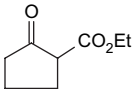
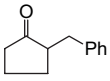
The active methylene compounds such as 1,3-diketones, 1,3-keto carboxylic esters, malononitrile and ethyl cyanoacetate were alkylated by alkyl halides catalyzed by this ionic liquid under microwave irradiation (Table 3). The alkyl halides included allyl, benzyl, methyl and butyl bromides/iodides. The open chain 1,3-ketones (entries 1–3) produced the monoalkylated products, whereas the cyclic diketones (entries 4–6 and 8) provided the dialkylated products in one stroke. Controlled experiments also did not produce any monoalkylated product. Similarly, malononitrile and ethyl cyanoacetate also furnished the dialkylated products (entries 9 and 10). Conventional heating at 80–100 °C for more than 12 h did not give satisfactory results. In a few reactions, the yields are 20–30% and no reaction was observed with many of these substrates. The β-keto ester (entry 11) during the process of

Table 2. Michael addition of thiols to conjugated acetylenic ketones catalyzed by [bmIm]OH

Entry	Acetylenic ketone	Thiol	Product	Time (min)	Yield[a] (%)	Ref.
1		EtSH		20	98	8a
2		*n*-BuSH		20	95	10
3		BnSH		20	95	8a
4				15	98	8a
5				20	95	8a
6		PhSH		15	98	11
7		EtSH		20	95	—

[a] Yields refer to those of pure isolated products characterized by IR, ^{1}H and ^{13}C NMR spectroscopic data.

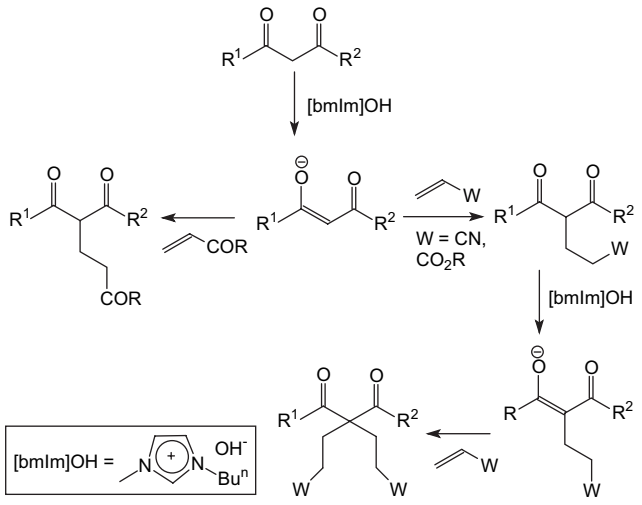
Table 3. Alkylation of active methylene compounds catalyzed by [bmIm]OH

Entry	Substrate	Alkyl halide	Product	Time (min)	Yield[a] (%)	Ref.
1		$PhCH_2Br$		5	87	12
2		^nBuI		4	89	—
3		$PhCH_2Br$		6	85	13
4		MeI		6	83	14
5				7	65	15
6				6	62	16
7		$PhCH_2Br$		4	95	9d
8		$PhCH_2Br$		5	81	17
9		$PhCH_2Br$		5	82	18
10		$PhCH_2Br$		6	85	9a
11		$PhCH_2Br$		5	92	19

[a] Yields refer to those of pure isolated products characterized by IR, ^1H and ^{13}C NMR spectroscopic data.

alkylation by this procedure underwent decarboxylation to give the corresponding alkylated ketone.

In general, all the reactions are clean and fast. During thia-Michael addition another ionic liquid [bmIm]Br was used as the reaction medium together with [bmIm]OH (10 mol %) to get better results. Without [bmIm]Br the reactions became vigorous and led to polymerization. In relatively larger scale (3 mmol and greater) reactions, the products were distilled directly from the reaction vessel, thus avoiding organic solvents totally in the process. The products were obtained in high purity. The ionic liquid has been reused for up to six runs without any loss of activity. Possibly, the reactions are going through the same course as in base catalyzed Michael additions and alkylations and the ionic liquid works here as base (Scheme 2). However, the reasons for bis-Michael additions with methyl acrylate and acrylonitrile (Table 1) and dialkylation on cyclic 1,3-diketones (Table 3) with this ionic liquid are not clear.



Scheme 2.

3. Conclusion

In conclusion, the procedure reported herein employed a basic and easily accessible ionic liquid, [bmIm]OH, which is efficient for Michael addition of active methylene compounds to conjugated alkenes, double conjugate addition of thiols to acetylenic ketones, and alkylation of 1,3-dicarbonyl and -dicyano compounds with alkyl halides, without a requirement for any other catalyst and organic solvent. This method offers marked improvements with regard to operational simplicity, reaction time, high isolated yields of products, greenness of the procedure, avoiding hazardous organic solvents and toxic catalysts. It thus provides a better and practical alternative to the existing procedures for these reactions.[7–9]

4. Experimental

4.1. General

The ionic liquid [bmIm]OH was prepared according to the procedure described in our earlier communication.[4] IR spectra were taken as thin films for liquid compounds and as KBr pellets for solids on a Shimadzu 8300 FTIR spectrophotometer. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ solution at 300 and 75 MHz, respectively (Bruker 300 DPX instrument).

4.2. General experimental procedure. Representative one for Michael addition of methyl acrylate with malononitrile (entry 21, Table 1)

Methyl acrylate (602 mg, 7.0 mmol) was added dropwise to a well stirred mixture of malononitrile (198 mg, 3.0 mmol) in [bmIm]OH (235 mg, 1.5 mmol) and the reaction mixture was stirred for 1.5 h until completion of the reaction (TLC). The product was then directly distilled out from the reaction mixture to provide pure Michael adduct (678 mg, 95%) as a colourless liquid. The compound was identified by good agreement of its spectroscopic data (IR, ^1H and ^{13}C NMR) with those reported.[7i]

This procedure was followed for all the reactions listed in Table 1. The products are mostly known compounds except

four products (entries 17, 22, 23 and 26, Table 1) and were easily identified by comparison of their spectroscopic data with those reported (Refs. in Table 1). The unknown products were characterized by their spectroscopic (IR, ^{1}H and ^{13}C NMR) data and elemental analysis. These data are provided below.

4.2.1. 4-Cyano-4-ethoxycarbonyl-heptanedioic acid dibutyl ester (entry 17, Table 1). Colourless liquid, IR (neat) 2260, 1739, 1452 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.90 (t, J=7.3 Hz, 6H), 1.24–1.39 (m, 7H), 1.54–1.63 (m, 4H), 2.29 (t, J=8.5 Hz, 4H), 2.66 (t, J=8.5 Hz, 4H), 4.08 (t, J=6.7 Hz, 4H), 4.26 (q, J=7.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.9, 19.0 (2C), 24.8 (2C), 30.1 (2C), 30.5 (2C), 32.0 (2C), 36.4, 63.1, 64.8 (2C), 117.9, 164.8, 171.4 (2C). Anal. Calcd for $C_{19}H_{31}O_6N$: C, 61.77; H, 8.46; N, 3.79. Found: C, 61.51; H, 8.21; N, 3.89.

4.2.2. 4,4-Dicyano-heptanedioic acid dibutyl ester (entry 22, Table 1). Colourless liquid, IR (neat) 2265, 1735, 1454 cm^{-1}; ^{1}H NMR δ 0.89 (t, J=7.3 Hz, 6H), 1.31–1.38 (m, 4H), 1.53–1.62 (m, 4H), 2.29 (t, J=8.5 Hz, 4H), 2.65 (t, J=8.5 Hz, 4H), 4.08 (t, J=6.7 Hz, 4H); ^{13}C NMR δ 15.0 (2C), 18.9 (2C), 30.2 (2C), 30.4 (2C), 32.6 (2C), 36.2, 65.1 (2C), 114.3 (2C), 117.4 (2C). Anal. Calcd for $C_{17}H_{26}O_4N_2$: C, 66.33; H, 8.13; N, 8.69. Found: C, 66.04; H, 8.02; N, 8.50.

4.2.3. 4,4-Dicyano-heptanedinitrile (entry 23, Table 1). Pale brown solid, mp 90–92 °C; IR (KBr) 2251, 2240, 1444 cm^{-1}; ^{1}H NMR δ 2.30 (t, J=4.3 Hz, 4H), 2.60 (t, J=4.3 Hz, 4H); ^{13}C NMR δ 13.5 (2C), 31.7 (2C), 35.4, 112.6 (2C), 116.3 (2C). Anal. Calcd for $C_9H_8N_4$: C, 55.05; H, 16.42; N, 28.53. Found: C, 54.82; H, 16.20; N, 28.44.

4.2.4. 1-(2-Butoxycarbonyl-ethyl)-2-oxo-cyclopentane-carboxylic acid ethyl ester (entry 26, Table 1). Colourless liquid, IR (neat) 1742, 1740, 1710 cm^{-1}; ^{1}H NMR δ 0.89 (t, J=7.4 Hz, 3H), 1.22 (t, J=7.1 Hz, 3H), 1.25–1.37 (m, 2H), 1.54–1.59 (m, 2H), 1.90–1.98 (m, 4H), 2.19–2.48 (m, 6H), 4.03 (t, J=6.6 Hz, 2H), 4.13 (q, J=7.1 Hz, 2H); ^{13}C NMR δ 13.4, 13.9, 19.0, 19.5, 28.3, 29.7, 30.5, 33.5, 37.8, 59.1, 61.4, 64.3, 170.2, 172.9, 214.3. Anal. Calcd for $C_{15}H_{24}O_5$: C, 63.36; H, 8.51. Found: C, 63.09; H, 8.48.

4.3. General experimental procedure. Representative one for Michael addition of ethane dithiol to phenyl acetylenic ketone (entry 1, Table 2)

The ionic liquid [bmIm]OH (15 mg, 10 mol %) was added dropwise to a well stirred mixture of phenyl acetylenic ketone (130 mg, 1 mmol), ethane dithiol (94 mg, 1 mmol) and [bmIm]Br (220 mg, 1 mmol), and the reaction mixture was stirred for 15 min till completion of reaction (TLC). The reaction mixture was extracted with ethyl acetate, washed with brine, dried (Na_2SO_4) and evaporated to leave the crude product, which was purified by short silica gel column chromatography to provide the pure adduct (219 mg, 98%) as a white solid. The product was identified by comparison of its IR, ^{1}H and ^{13}C NMR spectroscopic data with those reported.[8a] All the Michael addition products, except the one in entry 7, Table 2, are known compounds (Ref. in Table 2) and were characterized by good agreement of their spectroscopic (IR, ^{1}H and ^{13}C NMR) data with those reported. The product in entry 7 was characterized by its spectroscopic (IR, ^{1}H and ^{13}C NMR) data and elemental analysis. These data are provided below.

4.3.1. 2,3-Bis-ethylsulfanyl-1-phenyl-4-thiophene-2-yl-butane-1,4-dione (entry 7, Table 2). Brown solid, mp 80–82 °C; IR (KBr): 1435, 1690, 1702 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.08 (t, J=7.4 Hz, 3H), 1.20 (t, J=7.4 Hz, 3H), 2.53–2.70 (m, 4H), 4.78 (d, J=11.6 Hz, 1H), 4.96 (d, J=11.6 Hz, 1H), 7.18–7.74 (m, 5H), 7.89–8.17 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.0 (2C), 25.2, 25.9, 46.6, 48.4, 128.2, 128.4 (2C), 128.6 (2C), 132.1, 133.3, 134.3, 136.0, 143.1, 186.9, 193.1. Anal. Calcd for $C_{18}H_{20}O_2S_2$: C, 65.02; H, 6.06. Found: C, 64.88; H, 5.92.

4.4. General experimental procedure. Representative one for alkylation of dibenzoyl methane with benzyl bromide (entry 1, Table 3)

A mixture of dibenzoyl methane (224 mg, 1 mmol), benzyl bromide (171 mg, 1 mmol) and [bmIm]OH (250 mg) was subjected to microwave irradiation (CEM microwave reactor, 100 °C, 1.00 psi) for 5 min (TLC). The product was extracted with ethyl acetate (2×10 ml), washed with brine, dried (Na_2SO_4) and evaporated to leave a crude product, which was purified by a short column chromatography over silica gel (ethyl acetate/pet ether, 20:80) to provide the pure product, 2-benzyl-1,3-diphenyl-propane-1,3-dione (273 mg, 87%), as a white solid. The spectroscopic (IR, ^{1}H and ^{13}C NMR) data are in good agreement with those reported.[12] The remaining ionic liquid was dried under vacuum and reused for five reactions without any loss of efficiency. After five runs 50% of fresh ionic liquid was added to it and this was used again. This procedure was followed for all the reactions listed in Table 3. The products, except the one in entry 2, Table 3, are all known compounds and were identified by comparison of their spectroscopic data with those reported (Refs. in Table 3). The unknown compound (entry 2) was characterized by its spectroscopic (IR, ^{1}H and ^{13}C NMR) data and elemental analysis. These data were provided below.

4.4.1. 2-Butyl-1,3-diphenyl-propane-1,3-dione (entry 2, Table 3). Viscous liquid, IR (neat) 1693, 1664, 1446 cm^{-1}; ^{1}H NMR δ 0.87 (t, J=6.8 Hz, 3H), 1.32–1.43 (m, 4H), 2.09–2.16 (m, 2H), 5.25 (t, J=6.6 Hz, 1H), 7.38–7.43 (m, 4H), 7.47–7.54 (m, 2H), 7.96–7.99 (m, 4H); ^{13}C NMR δ 13.6, 22.5, 29.1, 30.2, 56.7, 126.9, 128.3 (4C), 128.6 (4C), 133.2 (2C), 135.9, 196.0 (2C). Anal. Calcd for $C_{19}H_{20}O_2$: C, 81.40; H, 7.19. Found: C, 81.32; H, 7.21.

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References and notes

1. (a) Welton, T. *Chem. Rev.* **1999**, *99*, 2071; (b) Wasserscheid, P.; Keim, W. *Angew. Chem., Int. Ed.* **2000**, *39*, 3773;

(c) Wilkes, J. S. *Green Chem.* **2002**, *4*, 73; (d) Zerth, H. M.; Leonard, N. M.; Mohan, R. S. *Org. Lett.* **2003**, *5*, 55; (e) Kumar, A.; Pawar, S. S. *J. Org. Chem.* **2004**, *69*, 1419; (f) Gu, D.-G.; Ji, S.-J.; Jiang, Z.-Q.; Zhou, M.-F.; Loh, T.-P. *Synlett* **2005**, 959.

2. (a) Boon, J. A.; Levinsky, J. A.; Pflug, J. I.; Wilkes, J. S. *J. Org. Chem.* **1986**, *51*, 480; (b) Harjani, J. R.; Nara, S. J.; Salunkhe, M. M. *Tetrahedron Lett.* **2002**, *43*, 1127; (c) Namboodiri, V. V.; Varma, R. S. *Chem. Commun.* **2002**, 342; (d) Sun, W.; Xia, C.-G.; Wang, H.-W. *Tetrahedron Lett.* **2003**, *44*, 2409; (e) Qiao, K.; Yakoyama, C. *Chem. Lett.* **2004**, *33*, 472; (f) Akaiyama, T.; Suzuki, A.; Fuchibe, K. *Synlett* **2005**, 1024.
3. (a) Ranu, B. C.; Das, A.; Samanta, S. *J. Chem. Soc., Perkin Trans. 1* **2002**, 1520; (b) Ranu, B. C.; Dey, S. S. *Tetrahedron Lett.* **2003**, *44*, 2865; (c) Ranu, B. C.; Dey, S. S.; Hajra, A. *Tetrahedron* **2003**, *59*, 2417; (d) Ranu, B. C.; Dey, S. S. *Tetrahedron* **2004**, *60*, 4183; (e) Ranu, B. C.; Das, A. *Aust. J. Chem.* **2004**, *57*, 605; (f) Ranu, B. C.; Jana, R.; Dey, S. S. *Chem. Lett.* **2004**, *33*, 274; (g) Ranu, B. C.; Jana, R. *Eur. J. Org. Chem.* **2005**, 775; (h) Ranu, B. C.; Banerjee, S. *J. Org. Chem.* **2005**, *70*, 4517; (i) Ranu, B. C.; Jana, R. *Adv. Synth. Catal.* **2005**, *347*, 1811; (j) Ranu, B. C.; Banerjee, S.; Das, A. *Tetrahedron Lett.* **2006**, *47*, 881.
4. Ranu, B. C.; Banerjee, S. *Org. Lett.* **2005**, *7*, 3049.
5. Xu, J.-M.; Liu, B.-K.; Wu, W.-B.; Qian, C.; Wu, Q.; Lin, X.-F. *J. Org. Chem.* **2006**, *71*, 3991.
6. Ranu, B. C.; Jana, R. *Eur. J. Org. Chem.* **2006**, 3767.
7. (a) Bergmann, E. D.; Ginsburg, D.; Pappo, R. *Org. React.* **1959**, *10*, 179; (b) Kobayashi, S. *Synlett* **1994**, 689; (c) Christoffers, J. *Eur. J. Org. Chem.* **1998**, 1259; (d) Srivastava, N.; Banik, B. K. *J. Org. Chem.* **2003**, *68*, 2109; (e) Shimizu, K. I.; Miyagi, M.; Kan-No, T.; Kodama, T.; Kitayama, Y. *Tetrahedron Lett.* **2003**, *44*, 7421; (f) Ranu, B. C.; Bhar, S.; Sarkar, D. C. *Tetrahedron Lett.* **1991**, *32*, 2811; (g) Ranu, B. C.; Bhar, S. *Tetrahedron* **1992**, *48*, 1327; (h) Zhang, Z.; Dong, Y.-W.; Wang, G.-W.; Komatsu, K. *Synlett* **2004**, 61; (i) Paganelli, S.; Schionato, A.; Botteghi, C. *Tetrahedron Lett.* **1991**, *32*, 2807; (j) Alvarez, S. G.; Hasegawa, S.; Hirano, M.; Komiya, S. *Tetrahedron Lett.* **1998**, *39*, 5209; (k) Laszlo, P.; Montaufier, M.-T.; Randriamahefa, S. L. *Tetrahedron Lett.* **1990**, *31*, 4867; (l) Kim, D. Y.; Huh, S. C.; Kim, S. M. *Tetrahedron Lett.* **2001**, *42*, 6299; (m) Bensa, D.; Constantieux, T.; Rodriguez, J. *Synthesis* **2004**, 923.
8. (a) Ranu, B. C.; Bhar, S.; Chakarborti, R. *J. Org. Chem.* **1992**, *57*, 7349; (b) Sneddon, H. F.; Gaunt, M. J.; Ley, S. V. *Org. Lett.* **2003**, *5*, 1147; (c) Smith, A. B., III; Adams, C. M.; Lodise Barbosa, S. A.; Degnan, A. P. *J. Am. Chem. Soc.* **2003**, *125*, 350.
9. (a) Katritzky, A. R.; Aurrecoechea, J. M. *Synthesis* **1987**, 342; (b) Rajamannar, T.; Palani, N.; Balasubramanian, K. K. *Synth. Commun.* **1993**, 3095; (c) Pickersgill, F.; Marchington, A. P.; Rayner, C. M. *J. Chem. Soc., Chem. Commun.* **1994**, 2597; (d) Bedekar, A. V.; Watanabe, T.; Tanaka, K.; Fuji, K. *Synthesis* **1995**, 1069; (e) Muthusamy, S.; Gnanaprakasam, B. *Tetrahedron Lett.* **2005**, *46*, 635.
10. Prilezhaeva, E. N.; Kikhelashvili, I. L. *Zh. Org. Khim.* **1973**, *9*, 1129.
11. Kuroda, H.; Tomita, I.; Endo, T. *Synth. Commun.* **1996**, *26*, 1539.
12. Barluenga, J.; Jordon, J.; Gotor, V. *J. Org. Chem.* **1985**, *50*, 802.
13. Algara, F.; Baldovi, M. V.; Garcia, H.; Miranda, M. A.; Primo, J. *Monatsh. Chem.* **1993**, *124*, 209.
14. Jacobson, B. M.; Soteropoulos, P.; Bahadori, S. *J. Org. Chem.* **1998**, *53*, 3247.
15. Kayaki, Y.; Koda, T.; Ikariya, T. *J. Org. Chem.* **2004**, *69*, 2595.
16. Yamamoto, Y.; Kinpara, K.; Saigoku, T.; Takagishi, M.; Okuda, S.; Nishiyama, H.; Itoh, K. *J. Am. Chem. Soc.* **2005**, *127*, 605.
17. Theobald, D. W. *Tetrahedron* **1978**, *34*, 1567.
18. Qian, F.; Mccusker, J. E.; Zhang, Y.; Main, A. D.; Chlebowski, M.; Kokka, M.; McElweewhile, L. *J. Org. Chem.* **2002**, *67*, 4086.
19. Kuwajima, I.; Nakamura, E.; Shimizu, M. *J. Am. Chem. Soc.* **1982**, *104*, 1025.