Available online at www.sciencedirect.com
SCIENCE DIRECT®
Tetrahedron Letters
Tetrahedron Letters 46 (2005) 2141–2145

Utilisation of 1,3-dialkylimidazolium-2-carboxylates as CO_2-carriers in the presence of Na^+ and K^+: application in the synthesis of carboxylates, monomethylcarbonate anions and halogen-free ionic liquids

Immacolata Tommasi* and Fabiana Sorrentino

Department of Chemistry, University of Bari, Campus Universitario, via Orabona 4, Bari 70126, Italy

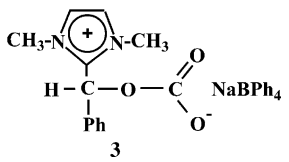
Received 1 September 2004; revised 18 January 2005; accepted 21 January 2005

Abstract—1,3-Dialkylimidazolium-2-carboxylate compounds have recently been fully characterised. Here we describe the utilisation of 1,3-dimethyl (**1a**) and 1-butyl-3-methyl-imidazolium-2-carboxylate (**1b**) in a carboxylation reaction with transfer of the CO_2 moiety to benzoylacetone and methanol for the synthesis, in high yield, of benzoylacetate and monoalkylcarbonate anions, respectively. Conversely, when compounds **1a** and **b** are reacted with carbonylic substrates lacking C–H active bonds, a product resulting from nucleophilic attack of the 1,3-dialkylimidazol-2-ylidene species on the carbonyl moiety is obtained. The reported reactions can find applications in organic synthesis and in the synthesis of halogen-free ionic liquids.

1. Introduction

There are very few examples in the literature for the synthesis and characterisation of 1,3-dialkylimidazolium-2-carboxylates. After the first description by Schossler and Regitz[1] of an 1,3-diphenylimidazolinium-2-carboxylate Kuhn et al. have reported the synthesis of 1,3-diisopropyl-4,5-dimethyl-imidazolium-2-carboxylate by reduction of the relevant 1,3-dialkylimidazol-thione with K and subsequent reaction of the intermediate carbene with CO_2.[2] More recently Tkatchenko and co-workers have published the unexpected formation of 1,3-dialkylimidazolium-2-carboxylates from the reaction of 1-alkyl imidazoles with dimethylcarbonate[3] while Louie and co-workers have reported the direct carboxylation of a 1,3-dialkylimidazol-2-ylidene with CO_2.[4]

Here we describe some aspects of the reactivity of 1,3-dimethylimidazolium-2-carboxylate (**1a**) and 1-butyl-3-methylimidazolium-2-carboxylate (**1b**) towards organic substrates in the presence of Na^+ and K^+ cations. Despite the thermal stability of compounds **1a** and **b** towards decarboxylation in solution we have found that, by reaction with methanol or benzoylacetone in the presence of Na^+ ($NaBF_4$, $NaBPh_4$) or K^+ (KPF_6) salts, an easy transfer of the CO_2 moiety to the organic substrate is observed to produce effectively monomethylcarbonate and benzoylacetate anions, respectively. Conversely, when 1,3-dimethylimidazolium-2-carboxylate (**1a**) is reacted with benzaldehyde in the presence of $NaBPh_4$, product **3** is formed which can be formally obtained by nucleophilic attack of a 2-ylidene species on the carbonyl group and transfer of CO_2 to the Alcoholate function.



3

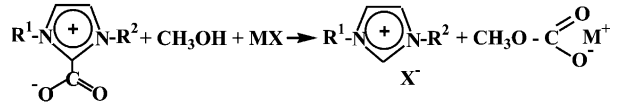
The reported reactions can find application in the synthesis of monomethyl carbonate, benzoylacetate anions and halogen-free ionic liquids.

Keywords: CO_2-carriers; Carboxylates; Carbonates; Ionic liquids.
* Corresponding author. Tel./fax: +39 080 5442083; e-mail: tommasi@chimca.uniba.it

0040-4039/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2005.01.106

2. Synthesis of alkylcarbonate anion and halogen-free ionic liquids

Both 1,3-dimethyl (**1a**) and 1-butyl-3-methyl-imidazolium-2-carboxylates (**1b**) are very stable towards decarboxylation at room temperature in most organic solvents (alcohols, DMF, acetone). At high temperatures (>100 °C) they behave differently according to the nature of the solvent,[5] but they are very stable when heated in ethylene glycol up to 140 °C.[6] Despite their thermal stability we have found that compounds **1a** and **b** readily react with dry methanol in the presence of a stoichiometric amount of sodium ($NaBF_4$) or potassium (KPF_6) salts quantitatively affording the corresponding 1,3-dialkylimidazolium salt and $CH_3OC(O)ONa$ according to Eq. 1.[7]



1a $R^1 = R^2 = CH_3$ **2a** $R^1 = R^2 = CH_3$

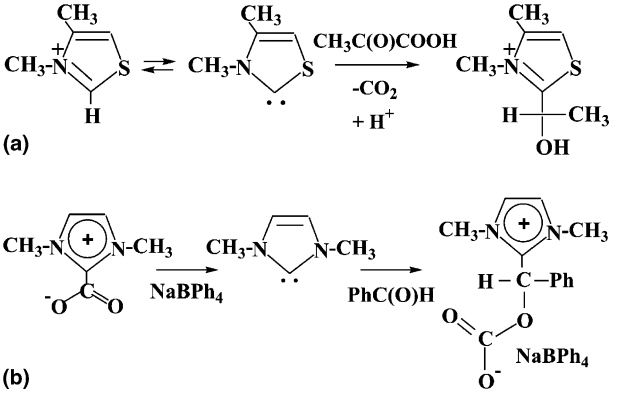
1b $R^1 = CH_3$, $R^2 = {}^nBu$ **2b** $R^1 = CH_3$, $R^2 = {}^nBu$

$M^+ = Na^+, K^+$

$X^- = BF_4^-, PF_6^-$

(1)

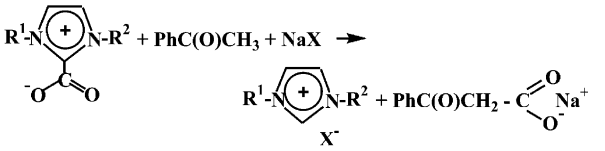
After solvent evaporation under reduced pressure, a mixture of salts is obtained. By addition of dry acetone the ionic liquids (i.e., 1,3-dimethylimidazolium tetrafluoroborate[8] or 1-butyl-3-methylimidazolium hexafluorophosphate[9]) can be quantitatively extracted from the salt mixture. It is worth noting that if the reaction reported in Eq. 1 is carried out using 1,3-dialkylimidazolium-2-carboxylates synthesised from 1-alkylimidazoles and DMC[3] (thus, avoiding the use of alkyl halides), the ionic liquid obtained is completely halogen-free.



Scheme 1. (a) Reactivity of 3,4-dimethylthiazolium cation, a model of thiamine.[16] (b) Reactivity of 1,3-dimethylimidazolium-2-carboxylate.

3. Carboxylation of benzoylacetone

Reacting 1,3-dimethyl-(**1a**) and 1-butyl-3-methylimidazolium-2-carboxylates (**1b**) at room temperature with benzoylacetone, in the presence of NaX ($X = BF_4^-$ or BPh_4^-), affords the corresponding ionic liquid and benzoylacetate through a quantitative transcarboxylation reaction shown in Eq. 2.[10]



1a $R^1 = R^2 = CH_3$ **2a** $R^1 = R^2 = CH_3$

1b $R^1 = CH_3$, $R^2 = {}^nBu$ **2b** $R^1 = CH_3$, $R^2 = {}^nBu$

$X^- = BF_4^-, BPh_4^-$

(2)

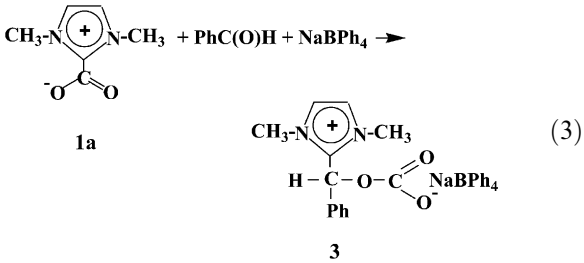
NMR analysis of the crude reaction mixture shows an almost quantitative conversion of reactants (>95%) and a high selectivity of the reaction (100%) as benzoylacetate and the ionic liquid are observed as the only reaction products. Yield in the carboxylation product is significantly lowered by the presence of adventitious water. After work-up of the crude reaction mixture the benzoylacetate salt can be obtained in 81% yield as a pure product and the corresponding acid can easily be obtained by acidification in water (at 4–5 °C) and extraction with ether.[11]

The time necessary for completion of the transcarboxylation reaction is limited by the solubility of salt in the reaction mixture. When **1b** is reacted with acetophenone and $NaBF_4$ (or KPF_6) in THF the reaction takes around 70 h for completion because of the low solubility of the salt in the reaction mixture. Conversely, when **1a** or **b** is reacted with acetophenone and $NaBPh_4$ in THF, the reaction are complete in 12 h.[12] As can be seen in Eq. 2, imidazolium-2-carboxylates **1a** and **b** act as CO_2-carriers, which is finally transferred to benzoylacetate.

We have also shown that 1,3-dialkylimidazolium-2-carboxylates **1a** and **b** can be synthesised from 1,3-dialkylimidazolium salts and CO_2.[13] Consequently, coupling the synthesis of the 1,3-dialkylimidazolium-2-carboxylate using CO_2 to the subsequent transfer of the CO_2 moiety to an organic substrate provides a novel route to benzoylacetic acid from benzoylacetone and CO_2.

4. Reactivity of 1,3-dimethylimidazolium-2-carboxylate towards benzaldehyde

Reacting 1,3-dimethylimidazolium-2-carboxylate with benzaldehyde at room temperature in the presence of a stoichiometric amount of $NaBPh_4$ allows product **3** to be isolated in 63% yield according to Eq. 3.[14]



1a **3**

(3)

Product **3** can be isolated as a complex ionic compound. An attempt to isolate the corresponding 2-(α-hydroxybenzyl)-1,3-dimethylimidazolium product by acidification led to decomposition.

It should be noted that product **3** is formally obtained by nucleophilic attack of an imidazol-2-ylidene species on the carbonyl carbon of benzaldehyde with subsequent transfer of the CO_2 moiety to the alcoholate functionality.

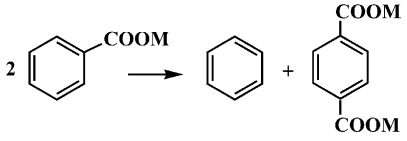
5. Intermediacy of an imidazolium-2-ylidene species

Whether the observed reactions (Eqs. 1–3) can be explained on the basis of an in situ generated 1,3-dialkylimidazol-2-ylidene reacting, respectively, as a base or nucleophile towards selected organic substrates, or whether a different reaction mechanism is involved, is a matter for detailed investigation. Some preliminary investigations have shown that reacting 1,3-dimethylimidazolium-2-carboxylate with $NaBPh_4$ in THF-d_8 did not indicate the presence of the free carbene (C2, 215 ppm as reported by Arduengo et al.[15]) nor that of free CO_2 in the ^{13}C NMR spectrum of the reaction solution [within the sensitivity allowed by the spectroscopic technique].

On the contrary, when compound **1b** was reacted with 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene in anhydrous THF-d_8 the carboxylate underwent exchange of CO_2 with the diisopropyl-imidazol-2-ylidene.[16] Based on this finding, the intermediacy of a free 2-ylidene species in the carboxylation of C–H active compounds might be proposed. By analogy with the reactivity of 1,3-dimethylimidazolium-2-carboxylate towards benzaldehyde (Eq. 3), thiazol-2-ylidenes react with pyruvic acid to give the 2-(α-hydroxyethyl)-3,4-dimethylthiazolium cation (Scheme 1a).[17]

Also in this case, based on this analogy, the intermediacy of a free 2-ylidene species able to attack the carbonylic carbon of benzaldehyde (Scheme 1b) affording product **3** can be proposed.

As far as the role of Group I cations is concerned, the activity of Na^+ and K^+ as promoters of a transcarboxylation reaction find a precedent in the transcarboxylation reaction of aromatic carboxylates (Henkel reaction)[18] even though this reaction takes place at a much higher temperature (370–465 °C).



(4)

$\mathbf{M} = Na^+, K^+$

In conclusion, we describe a new aspect of the reactivity of 1,3-dialkylimidazolium-2-carboxylates as CO_2-carriers. Compounds **1a** and **b** were observed to react selectively with benzoylacetone resulting in an enolisation–carboxylation reaction and behaving as nucleophiles towards benzaldehyde. The decarboxylation of compounds **1a** and **b** in CH_3OH (Eq. 1) together with the synthesis of 1-alkylimidazoles and dimethylcarbonate, allow the synthesis of halogen-free ionic liquids that may find wide application in catalysis.[19]

Acknowledgments

Financial support from Italian MIUR (PRIN 2003039774) and the University of Bari (Fondi di Ateneo 2002) is gratefully acknowledged.

References and notes

1. Schossler, W.; Regitz, M. *Chem. Ber.* **1974**, *107*, 1931.
2. Kuhn, N.; Steimann, M.; Weyers, G. *Z. Naturforsch.* **1999**, *54b*, 427.
3. Holbrey, J. D.; Reichert, W. M.; Tkatchenko, I.; Bouajila, E.; Walter, O.; Tommasi, I.; Rogers, R. D. *Chem. Commun.* **2003**, 28.
4. Duong, H. A.; Tekavec, T. N.; Arif, A. M.; Louie, J. *Chem. Commun.* **2004**, 112.
5. Bouajila, E.; Poinsot, D.; Tommasi, I.; Tkatchenko, I., '1,3-dialkylimidazolium-2-carboxylates: an entry to halogen-free ionic liquids, heterocarbenes and functionalised ionic ligands' *Green Solvents for Catalysis*, Bruchsal, Germany, October 15–19, 2002; p 58.
6. Stability of compounds **1a** and **b** in ethylene glycol. Approximately 0.170 g **1a** or **b** was solubilised in 5 mL of dry ethylene glycol in a two-necked Schlenck tube previously purged with dry nitrogen and equipped with a reflux system, a gas inlet and a pressure equalising valve. The clear solution was stirred at 140 °C for 5 h with N_2 bubbling and careful exclusion of air. Two samples (0.70 mL) of the solution was withdrawn before and after heating at 140 °C for 5 h. 30 μL of ethylene glycol dimethyl ether (standard purity) was added to each sample and the ^{13}C NMR spectra were recorded using the inverse gated decoupling technique. The ratio of the integrals of the signals of **1a** (35.0, 122.9, 136.1, 158.7 ppm) and of **1b** (13.10, 36.90, 122.15, 123.50, 140.38, 158.54 ppm) to that of the standard (70.4 and 57.5 ppm) was constant in the two samples (±3% accuracy) showing that no significant decomposition or decarboxylation of the compounds occurred by heating. It must be noted that significant decomposition of the compound was observed when compounds **1a** and **b** were heated at 140 °C in the presence of oxygen.
7. The synthesis of compounds **1a** and **b** as described in Ref. 3 leads to products containing around 5% of 4- and 5-carboxylate isomers. Recrystallisation from CH_3OH allows compounds **1a** and **b** to be obtained with >99% purity.
8. Procedure for the synthesis of 1,3-dimethylimidazolium tetrafluoroborate (**2a**) and sodium monomethylcarbonate. 1,3-Dimethylimidazolium-2-carboxylate (6.52 g, 0.046 mol), 5.10 g (0.046 mol) of $NaBF_4$ and 80 mL of dry CH_3OH were stirred as a slurry in a Schlenck tube previously purged with dry nitrogen, for 12 h at room temperature. The solvent was then evaporated under reduced pressure and the white solid residue was extracted with 5×40 mL of dry acetone. The residual CH_3O-C(O)ONa weighed 4.21 g (94.2% yield). The combined acetone fractions were dried under reduced pressure to

give 7.67 g (89.62% yield) of the ionic liquid 1,3-dimethylimidazolium tetrafluoroborate. *Characterisation of $CH_3OC(O)ONa$*: Anal. Calcd for $C_2H_3NaO_3$: C, 24.50; H, 3.08; Na, 23.45. Found: C, 24.20; H, 3.11; Na, 23.01; IR (nujol, KBr): 1631, 1457, 1190, 1089, 825 cm^{-1} (spectroscopic data were in full agreement with those of authentic samples). *Characterisation of 1,3-dimethylimidazolium tetrafluoroborate ionic liquid* (*2a*): Anal. Calcd for $C_5H_9BF_4N_2$: C, 32.65; H, 4.93; N, 15.23. Found: C, 32.35; H, 4.98; N, 15.09. The ionic liquid contained 36 ppm (w/w) of Na^+. ^1H NMR (500 MHz, acetone-d_6): δ 4.0 (s, 6H, CH_3), 7.64 (d, 2H, $^3J_{H-H}$ = 1.6 Hz, C_4–*H* and C_5–*H*), 8.96 (s, 0.7H due to partial exchange with acetone-d_6, C_2–*H*). Spectroscopic data were in full agreement with data reported in the literature Holbrey, J. D.; Seddon, K. R. *J. Chem. Soc., Dalton Trans.* **1999**, 2133.

9. Procedure for the synthesis of 1-butyl-3-methylimidazolium hexafluorophosphate (**2b**) and potassium monomethylcarbonate. 1-Butyl-3-methylimidazolium-2-carboxylate (7.1 g, 0.039 mol), 7.17 g (0.039 mol) of KPF_6 and 90 mL of dry CH_3OH were reacted in a Schlenck tube, previously purged with dry nitrogen. The reaction mixture was stirred at room temperature for 12 h. Potassium monomethylcarbonate (3.88 g, 87% yield) and 1-butyl-3-methylimidazolium hexafluorophosphate (7.99 g, 72% yield) were isolated following the procedure reported above (extraction of the ionic liquid using 5×40 mL of CH_3CN) and fully characterised. *Characterisation of 1-butyl-3-methylimidazolium hexafluorophosphate ionic liquid* (**2b**), Anal. Calcd for $C_8H_{15}PF_6N_2$: C, 33.81; H, 5.32; N, 9.86. Found: C, 33.64; H, 5.41; N, 9.75. The ionic liquid contains 29 ppm (w/w) of Na^+. ^1H NMR (500 MHz, acetone-d_6): δ 0.93 (m, 3H, CH_2–CH_3), 1.41 (m, 2H, CH_2–CH_3), 1.85 (m, 2H, CH_2–CH_2–CH_3), 3.99 (s, 3H, N_3–CH_3), 4.31 (m, 2H, N_1–CH_2), 7.62 (s, 1H, C_5–*H*), 7.73 (s, 1H, C_4–*H*), 8.90 (s, C_2–*H*). Spectroscopic data were in full agreement with data reported in the literature Billard, I.; Moutiers, Gilles; Labet, Alexandre; Al Azzi, A.; Gaillard, C.; Mariet, C.; Lutzenkirchen, K. *Inorg. Chem.* **2003**, *42*, 1726.
10. *Procedure for the synthesis of benzoylacetate (using $NaBF_4$)*: 1-butyl-3-methylimidazolium-2-carboxylate (6.55 g, 0.036 mol) were reacted under nitrogen with 3.95 g (0.036 mol) of $NaBF_4$ and 4.19 mL (0.036 mol) of benzoylacetone in dry THF (30 mL) at room temperature for 70 h. A dense suspension was obtained to which were added 50 mL of dry CH_3CN. The white solid isolated by filtration was washed with 3×30 mL of dry acetone, dried under reduced pressure and characterised as sodium benzoylacetate (5.53 g, 84% yield). Organic fractions were collected, dried in vacuo, extracted with 2×20 mL of toluene (to eliminate unreacted acetophenone) and dried in vacuo 6.89 g (84.8% yield) of 1-butyl-3-methylimidazolium tetrafluoroborate ionic liquid were isolated (characterised as reported before). *Characterisation of $PhC(O)CH_2C(O)ONa$*. Anal. Calcd for $C_9H_6NaO_3$: C, 58.07; H, 3.79; Na, 12.35. Found: C, 57.47; H, 3.84; Na, 12.09; IR (nujol, KBr): 1686, 1597 cm^{-1}; ^1H NMR (D_2O, 500 MHz): protons due to –CH_2– group were not observed because of fast exchange with D_2O, δ 7.44 (t, 2H, C*H*-*meta*-Ph, $^3J_{H-H}$ = 7.7 Hz), 7.57 (t, 1H, C*H*-*para*-Ph, $^3J_{H-H}$ = 7.48 Hz), 7.88 (d, 2H, C*H*-*ortho*-Ph, $^3J_{H-H}$ = 8.23 Hz); ^{13}C NMR (D_2O, 125 MHz): δ 50.01 (q, keto tautomer, *C*D_2, $^3J_{H-H}$ = 20.83 Hz), 130.18 (C-*meta*-Ph), 130.42 (C-*ortho*-Ph) 135.74 (C-*para*-Ph), 137.49 (C-*ipso*-Ph), 176.81 (CH–*C*(O)O^-), 201 (Ph–*C*(O)–CH_2).
11. *Synthesis of benzoylacetic acid*. Sodium benzoylacetate (4.80 g) was suspended in water at 4–5 °C and 35 mL of 10% H_2SO_4 was added to the suspension. The system was stirred for 10 min then extracted with 3×20 mL of Et_2O. The combined ether fractions were dried over Na_2SO_4, filtered and dried under reduced pressure. Benzoylacetic acid (3.75 g, 88% yield) were recovered. *Characterisation of benzoylacetic acid*. Anal. Calcd for $C_9H_8O_3$: C, 65.85; H, 4.91. Found: C, 65.19; H, 4.97; IR (nujol, KBr): 1649, 1610 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz,): δ 3.58 (s, 1.52H, CH_2 keto tautomer), 5.31 (s, 0.24H, C*H* enol tautomer), 7.16 (t, 2H, C*H*-*meta*-Ph, $^3J_{H-H}$ = 7.9 Hz), 7.28 (t, 1H, C*H*-*para*-Ph $^3J_{H-H}$ = 8.0 Hz), 7.64 (d, 2H, C*H*-*ortho*-Ph, $^3J_{H-H}$ = 8.0 Hz), 12.98 (br s, 0.24H, C–O*H* enol tautomer); ^{13}C NMR ($CDCl_3$, 125 MHz,): δ 45.47 (*C*H_2 keto tautomer), 86.52 (*C*H enol tautomer), 127.78 (C-*meta*-Ph), 128.09 (C-*ortho*-Ph), 133.14 (C-*para*-Ph), 136.34 (C-*ipso*-Ph), 168.75 (*C*OOH), 192.5 (C(O) carbonylic).
12. *Procedure for the synthesis of sodium benzoylacetate* (*using $NaBPh_4$*). 1,3-Dimethylimidazolium-2-carboxylate (6.32 g, 0.045 mol), 15.43 g (0.045 mol) of $NaBPh_4$, 5.3 mL (0.045 mol) of benzoylacetone and 70 mL of dry THF were placed in a Schlenck tube previously purged with dry nitrogen. The slurry was stirred at room temperature for 12 h during which time an abundant white solid was deposited. The solvent was reduced to approximately one half by evaporating in vacuo, then the product was precipitated with dry acetone. The filtered solid was washed with 2×10 mL of THF and dried in vacuo. Sodium benzoylacetate (6.12 g, 73% yield) was obtained.
13. (a) Tommasi, I; Sorrentino, F., Proceedings of the 14th International Symposium on Homogeneous Catalysis, Munich, Germany, July 5–9, 2004; 521; (b) Tommasi, I., forthcoming paper.
14. *Reaction of* **1a** *with benzaldehyde*. 1,3-Dimethylimidazolium-2-carboxylate (4.52 g, 0.032 mol), 11.03 g (0.032 mol) of $NaBPh_4$ and 3.3 mL (0.032 mol) of benzaldehyde were suspended in 45 mL of dry THF and the slurry was stirred at room temperature for 12 h. The solvent was then evaporated under reduced pressure and the solid residue was washed with 3×10 mL of THF. 70 mL of dry CH_3CN was added to the solid residue (to eliminate unreacted 1,3-dimethylimidaozolium-2-carboxylate) and it was then filtered. By evaporation of CH_3CN under reduced pressure 11.9 g (63% yield) of a light yellow solid residue which was characterised as product **3**. *Characterisation of product* **3**. Anal. Calcd for $C_{37}H_{34}BN_2NaO_3$: C, 75.52; H, 5.82; N, 4.76; Na, 3.91. Found: C, 74.93; H, 5.89; N, 4.71; Na, 3.83; IR (nujol, KBr): 1661, 1580, 1535, 1516, 1242, 1066, 837, 735, 713, 615, 606 cm^{-1}; ^1H NMR (CD_3CN, 500 MHz): δ 3.53 (s, 3H, *imidazolium*–CH_3), 6.85 (t, 4H, H-*para*, BPh4, $^3J_{H-H}$ = 7.2 Hz), 7.02 (t, 8H, H-*meta*-BPh4, $^3J_{H-H}$ = 7.8 Hz), 7.23 (s, 2H, C*4 imidazolium–H* and C*5 imidazolium–H*), 7.35 (m, 8H, H-*ortho*-BPh4), 7.58 (t, 2H, *meta*-Ph, $^3J_{H-H}$ = 7.8 Hz), 7.70 (t, 1H, *para*-Ph, $^3J_{H-H}$ = 6.2 Hz), 7.91 (d, 2H, *ortho*-Ph, $^3J_{H-H}$ = 7.0 Hz), 10.04 (s, 1H, C–*H*); ^{13}C NMR (CD_3CN, 125 MHz): δ 37.03 (s, imidazolium–*C*H3), 123.33 (s, C-*para*-BPh4), 127.0 (s, C-*meta*-BPh4), 129.4 (s, C-*meta*-Ph), 130.3 (s, C-*ortho*-Ph), 135.64 (s, C-*ortho*-BPh4), 135.71 (s, C4- and C5-*imidazolium*), 135.8 (s, C-*para*-Ph), 139.2 (s. C-*ipso*-Ph), 163.5 (q, C-*ipso*-BPh4, $^1J_{CB}$ = 49.3 Hz), 161.3 (O–*C*(O)O–), 196.89 (s, C–H).
15. Arduengo, A. J.; Dias, R.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1992**, *114*, 5530.
16. *Crossover experiment between 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene and compound* **1a**. Compound **1b** (0.050 g, 0.27 mmol) were suspended in 2.5 mL of anhydrous THF-d_8 and reacted, under nitrogen, with 0.059 g of 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (0.32 mmol).

The analysis of the ^{13}C NMR spectra of the reaction solution showed the appearance of signals at 215.5 ppm assigned to the C2 carbon of 1,3-dimethylimidazolium-2-ylidene and at 155.5 ppm due to the carboxylic carbon of the 1,3-diisopropyl-4,5-dimethylimidazolium-2-carboxylate. Signals at 205.9 ppm due to C2 of 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene and at 161.2 ppm due to –COO– of 1-butyl-3-methyl-imidazolium-2-carboxylate were also observed.

17. (a) Bordwell, F. G.; Satish, A. V.. *J. Am. Chem. Soc.* **1991**, *113*, 985; (b) Breslow, R. *J. Am. Chem. Soc.* **1958**, *80*, 3719; (c) Kluger, R. *Chem. Rev.* **1987**, *87*, 863.
18. McNelis, E. *J. Org. Chem.* **1965**, *30*, 1209.
19. (a) See for example: *Ionic liquids: industrial application for green chemistry.* ACS Symposium Series; Rogers, R. D., Seddon, K. R., Eds.; ACS: Washington, DC, 2002; p 818; (b) Dupont, J.; de Souza, P. A. Z. S. *Chem. Rev.* **2002**, *102*, 3667.