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ARTICLE

Stability and decarbonylation of 1,3-dialkyl-2-formylimidazolium perchlorate in solution

Hong-Xing Xin, Qi Liu, Hong Yan, and Xiu-Qing Song

Abstract: The stability of 1,3-dialkyl-2-formylimidazolium perchlorate **1** in solution was studied in detail and found to be related to its structure and the solvent character and temperature. **1** was stable in common solvents at room temperature and unstable in protic solvents under reflux. In protic solvents, such as H_2O, MeOH, EtOH, and AcOH, **1** decarbonylated into 1,3-dialkylimidazole perchlorates **2**, which was confirmed by ^{1}H NMR, ^{13}C NMR, HRMS, and X-ray spectroscopy. The decarbonylation of **1** was proposed to occur via its hemiacetal formed by the addition of solvents based on the tracking NMR spectra of **1** in deuterated reagents.

Key words: decarbonylation, solution stability, 2-formylimidazolium, imidazolium.

Résumé : On a étudié en détail la stabilité du perchlorate de 1,3-dialkyl-2-formylimidazolium **1** en solution et constaté qu'elle dépend de la structure du composé, ainsi que du caractère du solvant et de la température. **1** est stable dans les solvants communs à température ambiante et instable dans les solvants protiques sous reflux. Dans les solvants protiques, tels que H_2O, MeOH, EtOH et AcOH, **1** se décarbonyle pour former des perchlorates de 1,3-dialkylimidazole **2**, dont la présence a été confirmée par RMN ^{1}H, RMN ^{13}C, SMHR et spectrométrie de rayons X. L'examen des spectres RMN de **1** dans des solvants deutérés donne à penser que la décarbonylation de **1** a pour intermédiaire son hémiacétal formé par ajout de solvants. [Traduit par la Rédaction]

Mots-clés : décarbonylation, stabilité en solution, 2-formylimidazolium, imidazolium.

Introduction

Imidazoles have important functionalities in biological systems and are often used as building blocks in medicinal chemistry. Many compounds bearing this group have been widely studied due to their physiological activities.[1–6] Formylimidazolium salts are important synthons for incorporating a permanently cationic imidazolium group into a molecular framework. The utility of 1,3-dimethylformylimidazolium salt was reported in a variety of reactions, such as Knoevenagel and Wittig reactions, Schiff base formation, based-mediated electrophilic substitution, and oxidation, including the synthesis of the natural product norzooanemonin.[7] Formylimidazolium iodide was usually prepared by the formylation of 1,3-dimethylimidazolium iodide with ethyl formate[8] or dimethylformamide.[9] Furthermore, 2-formylimidazolium chloride was synthesized by the reaction of *N*,*N*′-di(tert-butyl)-1,4-diazabutadiene with HCl gas.[10] When preparing 1,3-dialkyl-2-formylimidazolium perchlorates **1** by the reaction of *N*,*N*′-dialkyl-1,4-diazabutadiene with $HClO_4$ in AcOH, **1** was unstable in solutions. However, few reports study the stability of the formylimidazolium perchlorates. Herein, the solution stability of **1** was investigated in common solvents and the structures of the decomposition products were identified by NMR, HRMS, and X-ray spectroscopy. A decomposition mechanism was proposed for the decarbonylation of **1** based on the tracking NMR spectra of **1** in deuterated reagents.

Results and discussion

The solution stability of **1** was studied and traced by HPLC in common solvents at room temperature and refluxing temperature. At room temperature for 1 day, **1** was stable in MeOH, EtOH, H_2O, $CHCl_3$, AcOEt, acetone, DMSO, and AcOH. At refluxing temperature for 12 h, **1** was also stable in $CHCl_3$, AcOEt, acetone, and DMSO but unstable in MeOH, EtOH, H_2O, and AcOH. The decomposition products of **1** were 1,3-dialkylimidazolium perchlorates **2** (Scheme 1). The structure of **2** was confirmed by NMR, HRMS, and X-ray spectroscopy. In the ^{1}H NMR spectra of **2**, the aldehyde proton signals disappeared at lower fields (δ 10.1–10.8 ppm). Taking compound **2a** as an example, its ^{1}H NMR spectrum (Fig. 1: H5) contains a singlet (s, 1H) at 9.17 ppm that was attributed to the proton at C2 of the imidazole ring. The signals of the two protons at C4 and C5 of the imidazole ring exhibited one doublet with a coupling constant of 1.2 Hz for structural symmetry. The two isopropyl groups showed one heptet (2H) at 4.81 ppm and one doublet (12H) at 1.62 ppm with the same coupling constant of 6.4 Hz for structural symmetry. In addition, the ^{13}C NMR spectrum of **2a** (Fig. 1: C5) displayed four signals (120.7 and 133.6 ppm corresponding to the carbons of the imidazole ring and 22.0 and 53.2 ppm ascribed to the isopropyl groups) and no C=O peak at approximately

Scheme 1. Decarbonylation of **1** into **2** in solvents.

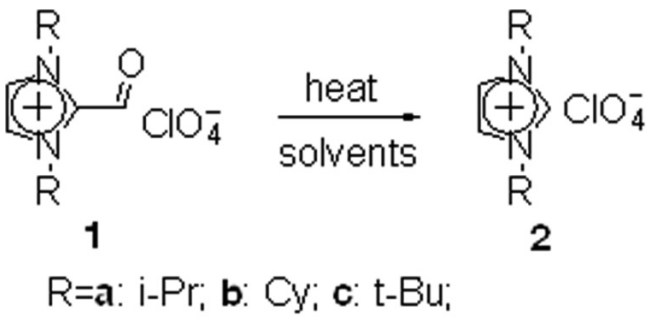

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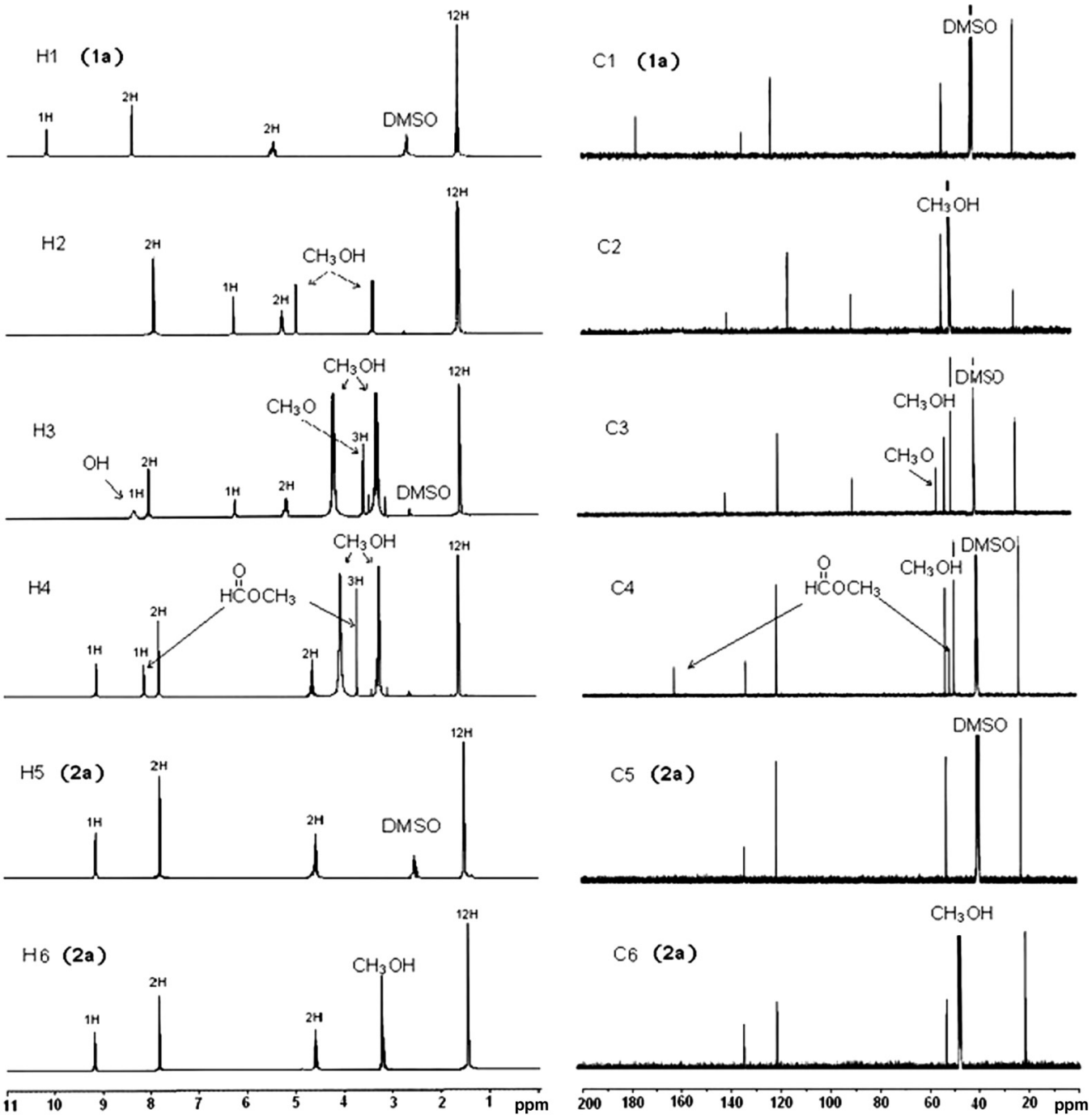
Fig. 1. ^{1}H NMR and ^{13}C NMR spectra at room temperature. (H1 and C1) **1a** in DMSO-d_6; (H2 and C2) **1a** in MeOH-d_4; (H3 and C3) **1a** and 0.05 mL of MeOH in 0.5 mL of DMSO-d_6; (H4 and C4) **1a** and 0.05 mL of MeOH in 0.5 mL of DMSO-d_6 after heating at 65 °C for 3 h; (H5 and C5) **2a** in DMSO-d_6; (**H6** and **C6**) **2a** in MeOH-d_4.



δ 177–183 ppm. The HRMS of **2a** (and that for all other compounds) revealed a strong peak at 153.1404 corresponding to $[M\text{-}ClO_4^-]^+$. Single-crystal X-ray diffraction of **2b** (Fig. 2) (CCDC No. 775890, see Supplementary material section) also proved that the decomposition products **2** were 1,3-dialkylimidazolium perchlorates.

The disappearance time of **1** under refluxing temperature is summarized in Table 1detected by HPLC. In protic solvents, 0.01 mol L^{-1} of **1** fully decomposed in 4.5 h and was more unstable in MeOH and H_2O than in EtOH or AcOH. The stability order of **1** was **1b**> **1a**> **1c**. The stability of **1** was mainly affected by imidazole structure and the solvent character besides the solvent temperature. The influence of the imidazole structure was embodied in the inductive effect of the nitrogen, the hyperconjugation effect, and the steric hindrance of *N*-substituents. The electron-attracting inductive effect of nitrogen in the imidazole ring is beneficial to the decarbonylation of **1** to **2**, which is in accordance with observations in other azoles.[11–12] The electron-donating effect and steric hindrance of *N*-substituents lead to the stability order of **1** as **1b**> **1a**> **1c** in the same solvent. The electron-donating effect of the Cy group in **1b** and the *i*-Pr group in **1a** weakens the electron-attracting effect of the imidazole ring and decreases the decarbonylation rate. The decarbonylation rates of **1b** and **1a** were greater

Fig. 2. ORTEP of **2b**, one of two independent molecules at 50% probability.

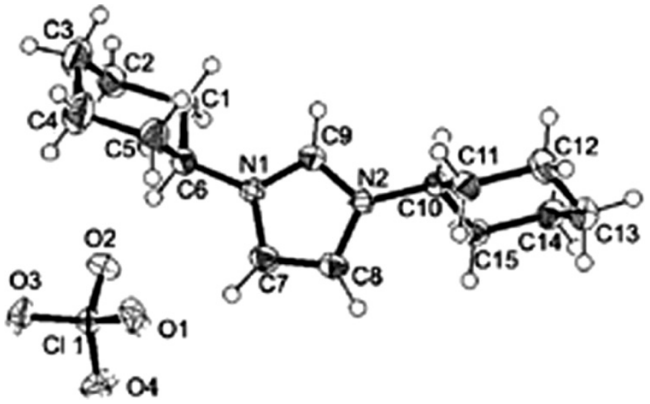


Table 1. Decomposition time[a] and rate[b] of **1** in solvents under refluxing temperature.

Compound	MeOH (rate)	EtOH (rate)	H_2O (rate)	AcOH (rate)
1a	1.5 (6.7)	3.5 (2.9)	1.5 (6.7)	3.5 (2.9)
1b	2.0 (5.0)	3.0 (3.3)	1.5 (6.7)	4.5 (2.2)
1c	1.0 (10.0)	1.5 (6.7)	1.0 (10.0)	2.5 (4.0)

[a]The full disappearance time (h) of 0.5 mmol of **1** in 50 mL of solvent was detected by HPLC.

[b]The rate (mmol L^{-1} h^{-1}) was the initial concentration of **1** divided by its disappearance time.

than that of **1c**. The steric hindrance of *N*-substituents hinders the attack of the solvent on the carbonyl. The greater steric hindrance of the Cy group relative to the *i*-Pr group slows the decarbonylation of **1b** relative to **1a**. The solvent structure is an obvious factor in the stability of **1**, which is stable in nonprotic solvent and unstable in protic solvent. Higher solvent polarities correspond to a more rapid decomposition of **1**. For example, **1a** was totally decomposed in AcOH for 3.5 h and in H_2O for 1.5 h with decarbonylation rates of 2.9 and 6.7 mmol L^{-1} h^{-1}, respectively.

To study the decarbonylation of **1** in MeOH, 5 mg of **1a** in DMSO-d_6 as the stable solvent, MeOH-d_4 as the unstable solvent, and DMSO-d_6 with 10% *v*/*v* MeOH were placed into individual 10 mL NMR tubes. After approximately 1 h, the ^{1}H NMR and ^{13}C NMR spectra were recorded as H1 and C1, H2 and C2, and H3 and C3, as shown in Fig. 1. Comparing the H2 and C2 spectra with the H1 and C1 spectra (all solvent signals are easily recognized and subtracted), the primary difference is that the signals of the aldehyde group (δ_H 10.11 ppm, 1H; δ_C 177.1 ppm) disappeared in MeOH-d_4 and new signals (δ_H 6.19 ppm, 1H; δ_C 88.9 ppm) appeared. Only one signal for the two protons at C4 and C5 of the imidazole ring existed at δ 7.83 ppm, and the total number of protons remained unchanged. These findings implied that new signals at δ_H 6.19 ppm and at δ_C 88.9 ppm come from the conversion of the aldehyde group, which was the only change. When MeOH was added to DMSO-d_6 for **1a**, the H3 spectrum relative to the H2 spectrum displayed greater intensities for a broad, low one-proton signal at δ 8.26 ppm and a sharp high three-proton singlet at δ_H 3.46 ppm. In the C3 spectrum relative to the C2 spectrum, one new signal appeared at δ_C 55.1 ppm. These changes indicated that the hemiacetal **3a** was formed by addition in which a MeOH molecule joined the aldehyde group of **1a** to form an OH group (δ_H 8.26 ppm) and a CH_3O group (δ_H 3.46 ppm, δ_C 55.1 ppm) in MeOH. The signals of the aldehyde group disappeared and new signals at δ_H 6.19 ppm and δ_C 88.9 ppm (HO-*CH*-OCH_3) appeared in MeOH. When the sample of **1a** in MeOH and DMSO-d_6 was heated at 65 °C for 3 h, the signals of methyl formate and **2a** were detected in H4 and C4 spectra. The signals at δ_H 3.65, δ_H 8.19, δ_C 49.0, and δ_C 162.7 ppm were attributed to methyl formate and the others to **2a** shown in H5 and C6 or H6 and C6 spectra. In MeOH, the mechanism of **1a** decarbonylating to **2a** was the addition of a MeOH molecule to **1a** to form the intermediate **3a** and the decarbonylation of **3a** to form **2a** and methyl formate (Scheme 2).

The decarbonylation of **1a** in H_2O was also investigated by the above method, and the spectra are shown in Fig. 3. The aldehyde group signals of **1a** vanished and new signals (δ_H 6.51 ppm, δ_C 82.0 ppm, HO-*CH*-OH) appeared in H7 and C7 spectra. When H_2O was added to the DMSO-d_6 for **1a**, a new low hydrogen signal (δ_H 7.96 ppm, 2H) appeared in the H8 spectrum relative to the H7 spectrum, and there was no new carbon signal in the C8 spectrum compared with the C7 spectrum. Those proved the formation of **3a**′ by addition of a H_2O molecule joining the aldehyde group of **1a** in which a H_2O molecule joined the aldehyde group of **1a** to form gem-diol (δ_H 7.96 ppm). The OH groups of the gem-diol that did not appear in the H7 spectrum due to addition by deuterated solvent (D_2O) and the $CH(OD)_2$ carbon appeared in the C7 spectrum at 82.0 ppm. When the sample of **1a** in H_2O and DMSO-d_6 was heated at 100 °C for 3 h, the signals of formic acid and **2a** were detected in H9 and C9 spectra. The signals at δ_H 8.11 ppm and δ_C 163.5 ppm were attributed to formic acid. The mechanism of **1a** decarbonylating to **2a** in H_2O was the same as in MeOH and the hemiacetal **3a**′ was the intermediate of decarbonylation of **1a** to **2a** (Scheme 3).

To investigate where the protons that end up on C2 of **2** come from, the H11 and H12 recorded as ^{1}H NMR spectra of **1a** in DMSO-d_6 with 10% *v*/*v* MeOH-d_4 and D_2O after heating for 3 h are shown in Fig. 4. Comparing the H11 and H12 spectra with the H4, H9, and H5 spectra, the singlet (s, 1H) at C2 of **2a** around 9.17 ppm did not appear and the aldehyde group signals of methyl formate and methanoic acid still existed. These indicate that the hydrogen at C2 of **2a** was deuterium and comes from solvents.

As observed from the differences between the NMR spectra of **1a** in MeOH-d_4 and MeOH, D_2O, and H_2O, **3a** and **3a**′ only exist in solvent and easily convert into **2a** under heating. When **1a** was dissolved in MeOH or H_2O and the solution dried in vacuo at room temperature, the residue was still **1a**. When it was dried under refluxing, the residue was **2a** but not **1a**. This result shows that **3** is stable at room temperature and unstable at higher temperatures such as heating. The thermal instability of **3** can further explain the stability of **1** in solution. It also indicates that the mechanism of decarbonylation of **1** includes the formation of hemiacetal **3** by the nucleophilic attack of protic solvents on the carbonyl of **1** and the decarbonylation of **3** to **2** at higher temperatures.

Conclusion

1,3-Dialkyl-2-formylimidazolium perchlorate **1** was stable in common solvents at room temperature and decarbonylated into 1,3-dialkylimidazole perchlorates **2** under reflux temperature in protic solvents. The main factors affecting the stability of **1** were the imidazole structure and the solvent character and temperature. By tracking the NMR spectra of **1** in deuterated reagents, the mechanism of decarbonylation of **1** includes the addition of **1** by solvent to form hemiacetal **3** and the decarbonylation of **3** to **2**.

Experimental

All chemicals were of commercial quality; the solvents were dried and purified by conventional methods. Melting points (uncorrected) were determined using an X-5 instrument. NMR spectra were recorded using a Bruker AVANCE 400 spectrometer. HRMS spectra were recorded using an Agilent G3250AA LC/MSD TOF mass spectrometer. HPLC instrument were the Agilent 1260 Infinty and column was the Agilent Eclipse Plus C18 (4.6 × 100 mm, 3.5 μm).

Scheme 2. Reaction of **1a** in MeOH.

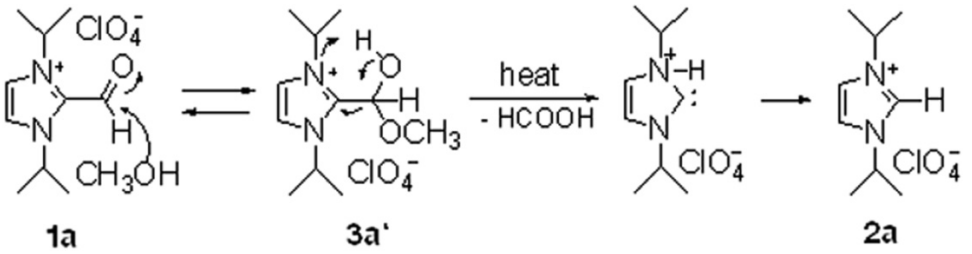
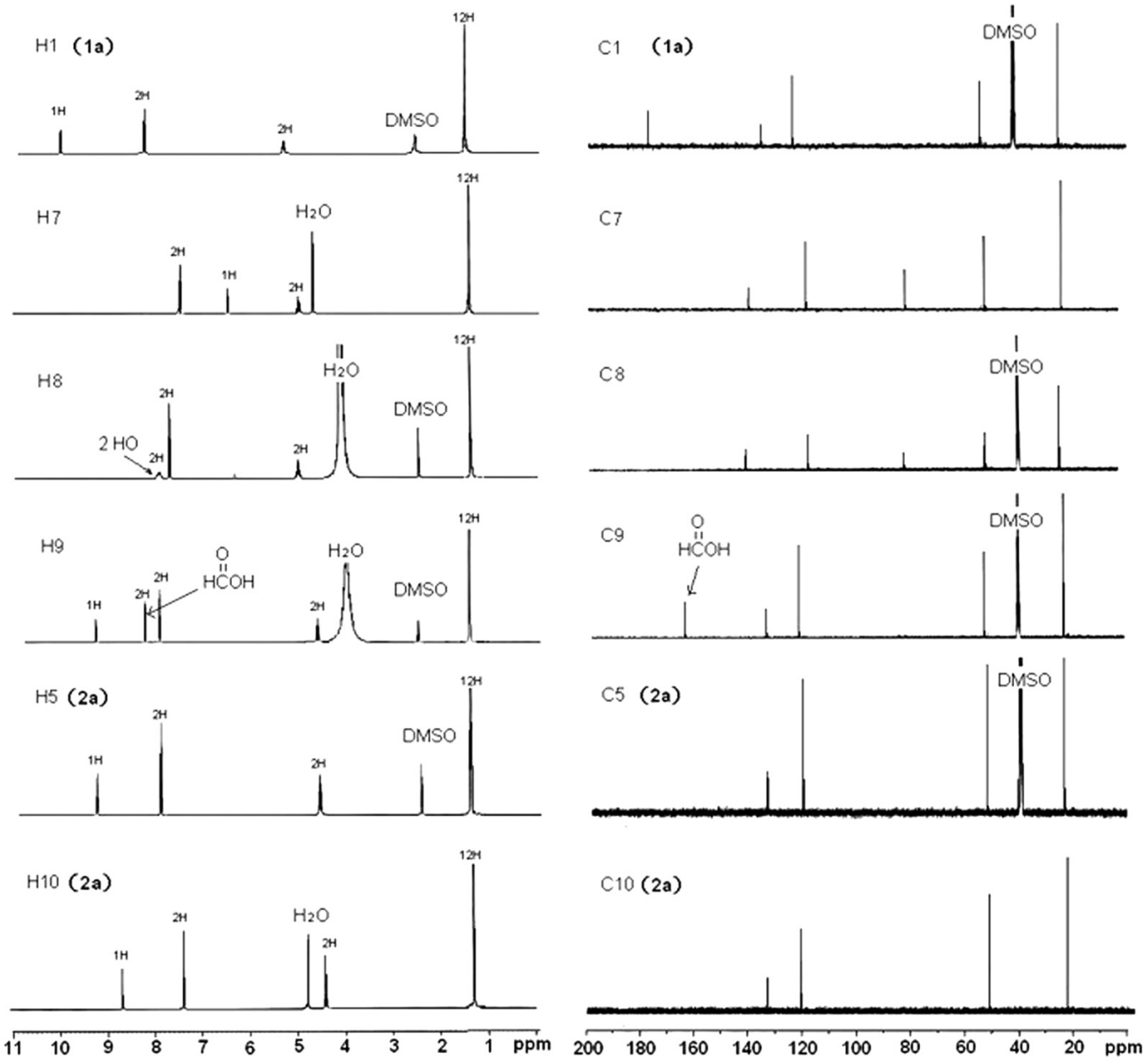


Fig. 3. ^{1}H NMR spectra and ^{13}C NMR spectra at room temperature. (H1 and C1) **1a** in DMSO-d_6; (H7 and C7) **1a** in D_2O; (H8 and C8) **1a** and 0.05 mL of H_2O in 0.5 mL of DMSO-d_6; (H9 and C9) **1a** and 0.05 mL of H_2O in 0.5 mL of DMSO-d_6 after heating at 100 °C for 3 h; (H5 and C5) **2a** in DMSO-d_6; (H10 and C10) **2a** in D_2O.



General synthetic procedure for 1,3-dialkyl-2-formylimidazolium perchlorate 1

A solution of $HClO_4$ in AcOH (5.0 mL, 1.0 N) was added to a solution of *N*,*N*′-disubstituted 1,4-diazabutadiene[13] (5 mmol) dissolved in AcOH (30 mL). The clear solution was allowed to stand overnight and the products crystallized. Filtering the resulting solid gave **1**. Caution should be used in the whole operation; higher temperatures should be avoided because of the hazard of $HClO_4$.

Scheme 3. Reaction of **1a** in H_2O.

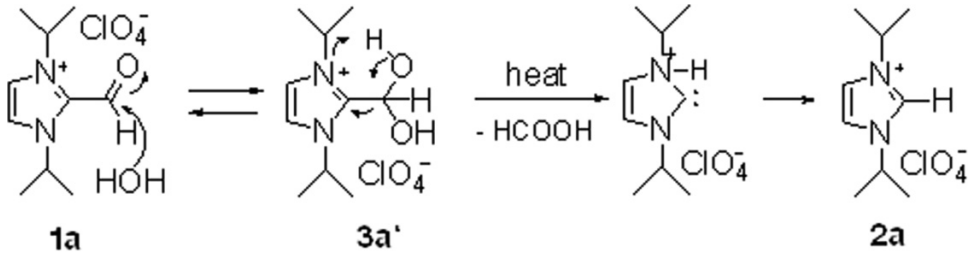
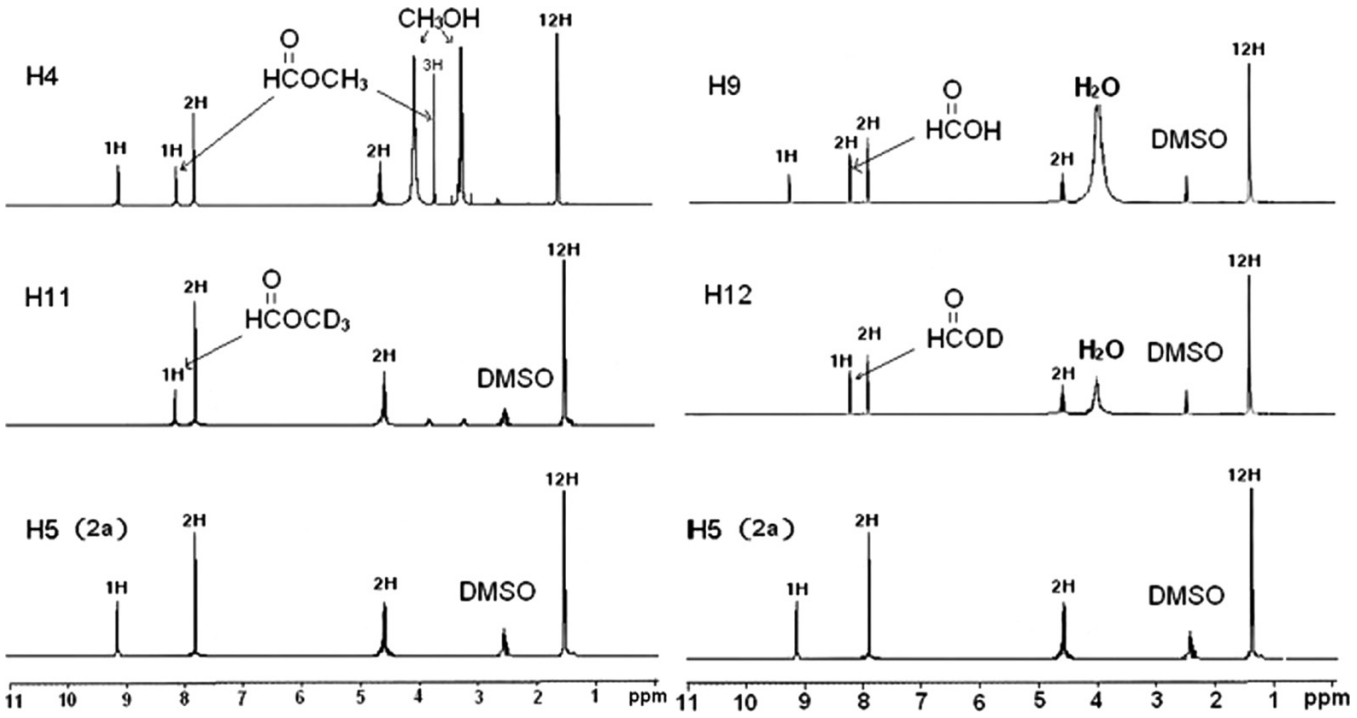


Fig. 4. ^1H NMR and ^{13}C NMR spectra at room temperature (H4) **1a** and 0.05 mL of MeOH in 0.5 mL of DMSO-d_6 after heating at 65 °C for 3 h; (H11) **1a** and 0.05 mL of MeOH-d_4 in 0.5 mL of DMSO-d_6 after heating at 65 °C for 3 h; (H5) **2a** in DMSO-d_6; (H9) **1a** and 0.05 mL of H_2O in 0.5 mL of DMSO-d_6 after heating at 100 °C for 3 h; (H12) **1a** and 0.05 mL of D_2O in 0.5 mL of DMSO-d_6 after heating at 100 °C for 3 h.



***1,3-Diisopropyl-2-formylimidazolium perchlorate* 1a**

Yield 57% as white crystals; mp 199–201 °C; ^1H NMR (400 MHz, DMSO-d_6) δ_H (ppm) 1.54 (d, J = 6.8 Hz, 12H), 5.14 (septet, J = 6.8 Hz, 2H), 8.01 (s, 2H), 10.11 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ_C (ppm) 22.7, 51.8, 122.3, 134.6, 177.1; ^1H NMR (400 MHz, MeOH-d_4) δ_H (ppm) 1.54 (d, J = 6.8 Hz, 12H), 5.19 (septet, J = 6.8 Hz, 2H), 6.19 (s, 1H), 7.83 (s, 2H); ^{13}C NMR (100 MHz, MeOH-d_4) δ_C (ppm) 21.5, 51.6, 88.9, 118.9, 141.5; ^1H NMR (400 MHz, D2O) δ_H (ppm) 1.38 (d, J = 6.8 Hz, 12H), 4.99 (septet, J = 6.8 Hz, 2H), 6.51 (s, 1H), 7.51 (s, 2H); ^{13}C NMR (100 MHz, D_2O) δ_C (ppm) 22.0, 51.4, 82.0, 118.9, 141.1; HRMS (ESI) m/z calcd.: 181.1341 for $C_{10}H_{17}N_2O$ [M-ClO_4^-]$^+$; found: 181.1338.

***1,3-Dicyclohexyl-2-formylimidazolium perchlorate* 1b**

Yield 89% as white crystals; mp 282–283 °C; ^1H NMR (400 MHz, DMSO-d_6) δ_H (ppm) 1.78 (m, 20H), 5.23 (m, 2H), 8.30 (s, 2H), 10.48 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ_C (ppm) 24.8, 25.2, 32.9, 58.4, 122.7, 134.7, 177.3; HRMS (ESI) m/z calcd.: 261.1967 for $C_{16}H_{25}N_2O$ [M-ClO_4^-]$^+$; found: 261.1940.

***1,3-Di-tert-butyl-2-formylimidazolium perchlorate* 1c**

Yield 61% as white solid; mp 132–133 °C; ^1H NMR (400 MHz, acetone-d_6) δ_H (ppm) 1.84 (s, 18H), 8.11 (s, 2H), 10.80 (s, 1H); ^{13}C NMR (100 MHz, acetone-d_6) δ_C (ppm) 29.9, 64.4, 122.1, 138.3, 182.4; HRMS (ESI) m/z calcd.: 181.1699 for $C_{11}H_{21}N_2$ [M-CO-ClO_4^-]$^+$; found: 181.1642.

General procedure for the synthesis for 1,3-dialkylimidazolium perchlorate 2

1 (1 mmol) was refluxed in EtOH (20 mL) and the reactions were considered complete when **1** was no longer detected by TLC. The solvent was removed in vacuo and the residue was the products **2**.

***1,3-Diisopropylimidazolium perchlorate* 2a**

Yield 97% as white solid; mp 117–119 °C; ^1H NMR (400 MHz, DMSO-d_6) δ_H (ppm) 1.62 (d, J = 6.4 Hz, 12H), 4.81 (heptet, J = 6.4 Hz, 2H), 7.87 (d, J = 1.2 Hz, 2H), 9.17 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ_C (ppm) 22.0, 53.2, 120.7, 133.6; ^1H NMR (400 MHz, MeOH-d_4) δ_H (ppm) 1.59 (d, J = 6.8 Hz, 12H), 4.67 (septet, J = 6.8 Hz, 2H), 7.76 (d, 2H, J = 1.6 Hz), 9.10 (s, 1H); ^{13}C NMR (100 MHz, MeOH-d_4) δ_C (ppm) 21.5, 53.2, 120.5, 133.2; ^1H NMR (400 MHz, D2O) δ_H (ppm) 1.37 (d, J = 6.8 Hz, 12H), 4.46 (septet, J = 6.8 Hz, 2H), 7.39 (d, 2H, J = 1.6 Hz), 8.68 (s, 2H); ^{13}C NMR (100 MHz, D_2O) δ_C (ppm) 21.9, 52.98, 120.4, 132.3; HRMS (ESI) m/z calcd.: 153.1392 for $C_9H_{17}N_2$ [M-ClO_4^-]$^+$; found: 153.1404.

***1,3-Dicyclohexylimidazolium perchlorate* 2b**

Yield 98% as white solid; mp 174–175 °C; ^1H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 1.25–2.21 (m, 20H), 4.35 (m, 2H), 7.47 (d, J = 1.6, 2H), 8.99 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C (ppm) 24.8, 33.3, 60.1, 77.1, 120.5, 133.2.

Table 2. Crystal data of **2b**.

Crystal	**2b**
Empirical formula	$C_{15}H_{25}C_6N_2O_4$
Formula mass	332.82
Colour, habit	Colourless, prism
Crystal dimensions (mm)	0.20 × 0.18 × 0.12
Crystal system	Monoclinic
Space group	$P2_1/c$
Z	2
a (Å)	12.088(2)
b (Å)	20.922(4)
c (Å)	13.598(3)
σ (°)	90
β (°)	94.57(3)
γ (°)	90
Collection ranges	$-14 \le h \le 14$, $-17 \le k \le 24$, $-16 \le l \le 16$
Temperature (K)	113(2)
Volume (Å^3)	3428.0(12)
$D_{calcd.}$ (Mg m^{-3})	1.290
Radiation	Mo Kα (λ = 0.71073 Å)
Absorption coefficient (μ) (mm^{-1})	0.242
Absorption correction	Semi-empirical from equivalents
F(000)	1424
θ range for data collection (°)	2.38–25.02
Observed refflections	22765
Independent reflections	6039 (R_{int} = 0.0386)
Data/restraints/parameters	6039/200/444
Goodnes-of-fit on F^2	1.065
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0506, wR_2 = 0.1323
R indices (all data)	R_1 = 0.0630, wR_2 = 0.1416
Extinction coefficient	0.0184(18)
Largest diff. peak and hole (e Å^{-3})	0.689 and −0.354

***1,3-Di-tert-butylimidazolium perchlorate* 2c**

Yield 97% as white solid; mp 244–246 °C; ^{1}H NMR (400 MHz, acetone-d_6) δ_H (ppm) 1.73 (s, 18H), 7.99 (s, 2H), 9.04 (s, 1H); ^{13}C NMR (100 MHz, acetone-d_6) δ_C (ppm) 29.3, 60.7, 121.0, 132.6; HRMS (ESI) m/z calcd.: 181.1699 for $C_{11}H_{21}N_2$ [M-ClO_4^-]$^+$; found: 181.1700.

***2-(Hydroxy(methoxy)methyl)-1,3-diisopropylimidazolium perchlorate* 3a**

^{1}H NMR (400 MHz, DMSO-d_6) δ_H (ppm) 1.44 (d, J = 6.8 Hz, 12H), 3.46 (s, 3H), 5.10 (heptet, J = 6.8 Hz, 2H), 6.15 (s, 1H), 7.98 (s, 2H), 8.26 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ_C (ppm) 22.4, 51.4, 55.1, 89.0, 119.7, 141.3.

***2-(Dihydroxymethyl)-1,3-diisopropylimidazolium perchlorate* 3a′**

^{1}H NMR (400 MHz, DMSO-d_6) δ_H (ppm) 1.39 (d, J = 6.8 Hz, 12H), 5.04 (heptet, J = 6.8 Hz, 2H), 6.38 (s, 1H), 7.74 (s, 2H), 7.96 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ_C (ppm) 22.6, 51.2, 82.3, 119.1, 142.9.

X-ray crystallography

Crystals of **2b** suitable for X-ray diffraction analysis were obtained by slow evaporation of an AcOEt solution of **2b** at room temperature. The single crystal X-ray diffraction measurement was carried out on a Rigaku Saturn CCD area-detector diffractometer at 113 (2) K using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) in the ω and φ scans scanning mode. An empirical absorption correction was applied using the SADABS program.[14] All structures were solved by direct methods using the SHELXS-97 program[15] and refined by full matrix least squares on F^2 using the SHELXL-97 program.[16] All of the hydrogen atoms were geometrically fixed using the riding model. Details of crystal data, data collections, and structure refinements are summarized in Table 2. 200 Restraints used in the least-square refinement were attributed solely to the disordered anion. The data are sufficient for confirmation of identity.

Stability analytical procedure

The HPLC was equipped with a diode array detector set at 267 nm and autosampler. Reversed-phase chromatography was used with a mobile phase of 30% acetonitrile and 70% 0.1 mol L^{-1} sodium acetate buffer solution (pH 4.3), flow rate of 1.0 mL min^{-1}, column temperature of 25 °C, and injection volume of 5 μL. Samples were injected directly into the HPLC at intervals of 0.5 h. The decomposition time was calculated by the signal disappearance of **1**. Retention time of **1** was around 3.5 min and of **2** was around 2.5 min.

Supplementary material

Supplementary data are available with the article through the journal Web site at http://nrcresearchpress.com/doi/suppl/10.1139/cjc-2012-0497. CCDC-775890 contains the supplementary crystallographic data for this paper. These data can be obtained, free of charge, via http://www.ccdc.cam.ac.uk/conts/retrieving.html.

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