

NOTE

Synthesis of Chiral Geminal Dicationic Ionic Liquid

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(Received: 21 September 2011;

Accepted: 21 June 2012)

AJC-11651

A series of chiral imidazolium ionic liquids (**3a-c**) containing one chiral carbon were synthesized by using natural amino acid, then reacted with 1,6-dibromohexane to obtain a series of chiral geminal dicationic ionic liquid (**5a-c**), the structures of the synthesized compounds were determined by IR, ¹H NMR, ¹³C NMR and the study for their application is under way.

Key Words: Chiral imidazolium ionic liquids, Chiral geminal dicationic ionic liquid, Synthesize, Characterization.

Along with the rapid development of chirality science, chiral ionic liquids are becoming increasingly important for research in synthesis¹⁻⁴, catalysis⁵ and separation^{6,7} by their unique physical properties and chemical properties. Most chiral ionic liquids reported are monocationic ionic liquids, which have low thermal stability, while much work focused on geminal dicationic ionic liquids because their high thermal stabilities⁸, but there is no report on chiral geminal dicationic ionic liquids.

It is well known that it is efficient way to get chiral ionic liquid by introducing chiral compounds^{6,9}. Natural amino acid is a kind of chiral source and it can be easy to obtain. Bao *et al.*¹⁰, synthesized chiral ionic liquids from the natural amino acids, which decomposed at > 180 °C.

In this work, a series of chiral imidazolium ionic liquids (**3a-c**) containing one chiral carbon were synthesized by using natural amino acid, then reacted with 1,6-dibromohexane to obtain a series of high stability chiral geminal dicationic ionic liquid (**5a-c**), the structures of the synthesized compounds were determined by IR, ¹H NMR, ¹³C NMR and the study for their application research in synthesis and separation is under way.

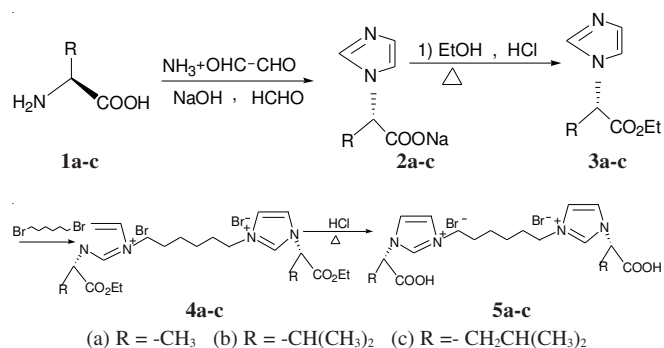
All the chemical reagents used are of analytical pure grade and 1,6-dibromohexane was distilled again. **3a-c** were synthesized according to the literature procedures¹⁰.

TLC analyses were carried out on silica gel plates, using dichloromethane (5 parts)/methanol (1 parts). IR (KBr) spectra (ν cm⁻¹) were obtained on Nicolet AVATAR 370 spectrometer, ¹H NMR, ¹³C NMR spectra were taken on a Avance 400 NMR spectrometer, using TMS as internal standard. The specific

rotations were measured on an Optical Instrument Ltd. WZZ-ZS polarimeter made in Shanghai Jinke. The melting point of the ionic liquid were determined using NJY2-DZ3339 Differential Scanning calorimeter (Beijing). Typical methods involved using a 10 °C/min temperature ramp to determine and identify the thermal transitions.

General procedure

Preparation of chiral geminal dicationic ionic liquid 5a-c: Synthetic route of chiral geminal dicationic ionic liquid **5a-c** can be seen in **Scheme-I** and **3a-c** were synthesized according to the literature procedures⁷.



Scheme-I: Synthetic route of chiral geminal dicationic ionic liquid

Procedure for the synthesis of **5a-c**: 0.025 molar 1,6-dibromohexane and 0.05 molar **3a** were reacted under the protection of N₂ at 70 °C for 4 h. TLC followed the track of reaction cooled in the natural condition and washed with 200

mL ethyl acetate four times, when reaction solution changed into viscous materials, evaporated solvent and vacuum drying 72 h to get light yellow solid **4a**, which refluxing in 20 mL concentrated hydrochloric acid **4h**, evaporated solvent under reduced pressure to obtain crude product and then recrystallized to afford the products. All the products were determined by ^1H and ^{13}C NMR (Tables 1 and 3). The physical data are given in Table-2.

TABLE-1
 ^1H NMR SPECTRA OF COMPOUNDS **4a-c**, **5a-c**

Compound	^1H NMR, δ (ppm)
4a	7.58 (s, 2H), 7.08 (s, 2H), 7.02 (s, 2H), 4.90-4.92 (q, $J = 8\text{Hz}$, 2H), 4.32-4.35 (q, $J = 12\text{Hz}$, 4H), 3.71-3.78 (m, 4H), 1.86-1.94 (m, 4H), 1.64-1.66 (d, $J = 8\text{Hz}$, 6H), 1.31-1.35 (m, 4H), 1.28-1.30 (t, $J = 8\text{Hz}$, 6H).
4b	7.62 (s, 2H), 7.10 (s, 2H), 7.07 (s, 2H), 4.78-4.80, (br, 2H), 4.26-4.28 (m, $J = 8\text{Hz}$, 4H), 3.78-3.84 (m, 4H), 2.41-2.46 (m, 2H), 1.88-1.95 (m, 4H), 1.28-1.30 (t, $J = 8\text{Hz}$, 6H), 1.31-1.35 (m, 4H), 1.00-1.02 (d, $J = 9\text{Hz}$, 6H), 0.79-0.82 (d, $J = 12\text{Hz}$, 6H)
4c	7.68 (s, 2H), 7.11(s, 2H), 7.06 (s, 2H), 4.72-4.74 (d, $J = 8\text{Hz}$, 2H), 4.33-4.38 (m, 4H), 3.76-3.80 (m, 4H), 1.94-1.96 (t, $J = 8\text{Hz}$, 4H), 1.82-1.91 (m, 4H), 1.37-1.44 (m, 2H), 1.32-1.35 (m, 4H), 1.25-1.28 (t, $J = 12\text{Hz}$, 6H), 0.91-0.92 (d, $J = 4\text{Hz}$, 6H), 0.88-0.89 (d, $J = 4\text{Hz}$, 6H).
5a	8.89 (s, 2H), 7.37(s, 2H), 7.48(s, 2H), 4.85-4.87 (q, $J = 8\text{Hz}$, 2H), 3.72-3.78 (m, 4H), 1.86-1.95(m, 4H), 1.54-1.56(d, $J = 8\text{Hz}$, 6H), 1.28-1.30(m, 4H).
5b	9.01(s, 2H), 7.68(s, 2H), 7.67(s, 2H), 4.80-4.84, (br, 2H), 3.73-3.80 (m, 4H), 2.21-2.26(m, 2H), 1.87-1.95(m, 4H), 1.29-1.33(m, 4H), 1.06-1.09(d, $J = 9\text{Hz}$, 6H), 0.80-0.84(d, $J = 12\text{Hz}$, 6H)
5c	8.84(s, 2H), 7.41(s, 2H), 7.46(s, 2H), 4.78-4.80 (d, $J = 8\text{Hz}$, 2H), 3.75-3.78(m, 4H), 1.83-1.85 (t, $J = 8\text{Hz}$, 4H), 1.82-1.91(m, 4H), 1.43-1.49(m, 2H), 1.30-1.34(m, 4H), 0.80-0.82(d, $J = 8\text{Hz}$, 6H), 0.87-0.88(d, $J = 4\text{Hz}$, 6H).

^1H NMR spectra were taken in CDCl_3 (**4a-c**), D_2O (**5a-c**), using TMS as internal standard.

TABLE-2
MELTING POINTS AND α OF **4a-c**, **5a-c**

Compound	T of solid/liquid transformation ($^{\circ}\text{C}$)	$[\alpha]_{\text{D}}^{25}$
4a	147	+17.4 (C2.0 %, CH_3OH)
4b	140	-18.1 (C2.0 %, CH_3OH)
4c	134	+16.5 (C2.0 %, CH_3OH)
5a	197	+9.4 (C2.0 %, CH_3OH)
5b	191	-20.3 (C2.0 %, CH_3OH)
5c	185	+18.4 (C2.0 %, CH_3OH)

TABLE-3
 ^{13}C NMR SPECTRA OF COMPOUNDS **4a-c**, **5a-c**

Compound	^{13}C NMR, δ (ppm)
4a	14.8, 15.7, 27.2, 30.1, 54.5, 65.1, 68.2, 122.8, 123.0, 137.0, 170.2
4b	13.81, 18.4, 25.7, 27.3, 30.4 54.8, 63.58, 79.2, 120.5, 123.0, 137.8, 171.9
4c	13.6, 22.9, 23.7, 27.1, 30.2, 34.3, 42.3, 54.2, 59.5, 69.6, 122.6, 123.3, 137.0, 171.4
5a	15.0, 27.3, 30.3, 54.8, 72.4, 122.8, 123.6, 137.3, 172.2
5b	18.2, 25.2, 27.6, 30.5, 55.0, 79.2, 120.3, 123.4, 137.0, 172.2
5c	22.9, 23.7, 27.1, 30.1, 34.6, 42.3, 54.9, 69.6, 122.8, 123.0, 137.4, 172.2

Chiral geminal dicationic ionic liquid 5a-c: Thermogravimetric analysis experiment showed that chiral *geminal* dicationic ionic liquid **5a-c** have high thermal stabilities and will not decompose more than 200 $^{\circ}\text{C}$ and their solubility experiment showed (Table-2) that chiral *geminal* dicationic ionic liquid **5a-c** are soluble in water and other polar solvent.

Conclusion

In summary, chiral *geminal* dicationic ionic liquid (**5a-c**) can be easily prepared by the reaction of chiral imidazolium ionic liquids with 1,6-dibromohexane. All the structures of the new compounds were characterized by IR, ^1H and ^{13}C NMR. Further investigations for their application is under way.

ACKNOWLEDGEMENTS

This work is supported by the Hunan Education Department (09C258).

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