Synthesis of Chiral Geminal Dicationic Ionic Liquid from Amino Acids

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(Received: 21 August 2012;

Accepted: 27 May 2013)

AJC-13557

Chiral imidazolium ionic liquids (**3**) from amino acid were synthesized when reacted with 1,2-dibromoethane, 1,3-dibromopropane, 1,4-dibromobutane, 1,6-dibromohexane and 1,9-dibromononane, respectively, to obtain a series of chiral *geminal* dicationic ionic liquid (**5**). The structures of the synthesized compounds were determined by IR, ¹H and ¹³C NMR, this method for the synthesis of chiral *geminal* dicationic ionic liquid is simple and rapid with high yield and the study for their application is under way.

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

INTRODUCTION

Since the first report of *geminal* dicationic ionic liquids in 2003¹, much effort has been devoted to the *geminal* dicationic ionic liquids because their superior physical properties compared to traditional monocationic ionic liquids². The application as solvents in high-temperature reactions³, novel high-temperature lubricants^{4,5}, ultrastable separation phases⁶ and dye sensitized solar cells^{7,8} have been reported.

It is well known that the chiral monocationic ionic liquids are attractive due to their potential for asymmetric synthesis^{9,10},

gas chromatography¹¹, optical resolution of racemates¹², stereo selective polymerization¹³. But there is no report on the synthesis and application of chiral *geminal* dicationic ionic liquids.

In this work, chiral imidazolium ionic liquids were designed from the natural amino acid, then reacted with 1,2-dibromoethane, 1,3-dibromopropane, 1,4-dibromobutane, 1,6-dibromohexane and 1,9-dibromononane, respectively, to obtain a series of chiral *geminal* dicationic ionic liquid (**Scheme-I**), 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.

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

EXPERIMENTAL

All the chemical reagents used are of analytical pure grade, 1,2-dibromoethane, 1,3-dibromopropane, 1,4-dibromobutane, 1,6-dibromohexane and 1,9-dibromononane was distilled again. Chiral imidazolium ionic liquids **3** from amino acid were synthesized according to the literature procedures¹⁴ and the products were determined by IR, ¹H NMR.

Melting points were recorded on a digital microscope are uncorrected. IR (KBr) spectra (ν cm⁻¹) were obtained on Nicolet AVATAR 370 spectrometer, ¹H and 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.

Procedure for the synthesis of chiral geminal dicationic ionic liquid (5): 0.25 molar of 1,2-dibromoethane, 1,3-dibromopropane, 1,4-dibromobutane, 1,6-dibromohexane and 1,9-dibromononane, respectively, reacted with 0.5 molar **3** under the protection of N₂ at room temperature then all the products were purified by extraction by 200 mL ethyl acetate four times when reaction solution changed into viscous and vacuum drying 72 h to get product **4**, which on refluxing in 20 mL concentrated hydrochloric acid for 4 h, evaporated solvent under reduced pressure to obtain crude products and then recrystallized to afford the products **5**.

RESULTS AND DISCUSSION

Melting points and optical activity of chiral geminal dicationic ionic liquid: Generally speaking, most ionic liquid are low melting, called room temperature ionic liquids, but the synthesized chiral *geminal* dicationic ionic liquid **5** have high melting (Table-1) and with the linkage chains increase, the melting points decrease.

TABLE-1
MELTING POINTS AND OPTICAL ACTIVITY OF **5**

Compound	T (°C)	$[\alpha]_D^{25}$
5a₂	218	+7.4(C2.0 %, CH ₃ OH)
5a₃	211	+7.8(C2.0 %, CH ₃ OH)
5a₄	205	+8.3(C2.0 %, CH ₃ OH)
5a₆	197	+9.4(C2.0 %, CH ₃ OH)
5a₉	164	+10.6(C2.0 %, CH ₃ OH)
5b₂	224	-18.4 (C2.0 %, CH ₃ OH)
5b₃	216	-18.9(C2.0 %, CH ₃ OH)
5b₄	208	-19.4(C2.0 %, CH ₃ OH)
5b₆	201	-20.3(C2.0 %, CH ₃ OH)
5b₉	171	-22.8(C2.0 %, CH ₃ OH)

^aMelting points were recorded on a digital microscope and are uncorrected.

Synthesis of chiral geminal dicationic ionic liquid: The synthesis for chiral *geminal* dicationic ionic liquid **5** is easy to purify and have high yields and the products were determined by IR, ¹H NMR (Table-2), ¹³C NMR (Table-3). Compounds **5** in IR showed absorption at 3424 cm⁻¹ (-OH), 1736 (C=O), 1629, 1579 ((imidazole).

Solubility of chiral geminal dicationic ionic liquid: Great attention has been paid to the ionic liquid as a new type of green solvent. The solubility of the synthesized chiral

TABLE-2
¹H NMR SPECTRA OF COMPOUNDS **5**

Compound	¹ H NMR, δ (ppm)
5a₂	8.76 (s, 2H), 7.40(s, 2H), 7.34(s, 2H), 4.82(q, 2H), 3.72 (t, 4H), 1.60(d, 6H).
5a₃	8.77(s, 2H), 7.43(s, 2H), 7.34(s, 2H), 4.80, (q, 2H), 3.80 (t, 4H), 1.71 (m, 2H), 1.62(d, 6H).
5a₄	8.84(s, 2H), 7.46(s, 2H), 7.41(s, 2H), 4.78 (d, 2H), 3.76 (t, 4H), 1.75 (m, 4H), 1.61(d, 6H).
5a₆	8.89(s, 2H), 7.48(s, 2H), 7.37(s, 2H), 4.87(q, 2H), 3.78 (t, 4H), 1.86(m, 4H), 1.56(d, 6H), 1.30(m, 4H).
5a₉	8.85(s, 2H), 7.44(s, 2H), 7.35(s, 2H), 4.88(q, 2H), 3.79 (t, 4H), 1.88(m, 4H), 1.58(d, 6H), 1.33-1.40(m, 10H).
5b₂	8.76(s, 2H), 7.40(s, 2H), 7.36(s, 2H), 4.82(q, 2H), 3.72 (t, 4H), 2.22(m, 2H), 1.01 (d, 6H), 0.80 (d, 6H).
5b₃	8.76(s, 2H), 7.42(s, 2H), 7.38(s, 2H), 4.81, (q, 2H), 3.79 (t, 4H), 2.22(m, 2H), 1.73 (m, 2H), 1.02 (d, 6H), 0.84 (d, 6H).
5b₄	8.87(s, 2H), 7.48(s, 2H), 7.42(s, 2H), 4.80 (d, 2H), 3.78 (t, 4H), 2.22(m, 2H), 1.76 (m, 4H), 1.04 (d, 6H), 0.87 (d, 6H).
5b₆	9.01(s, 2H), 7.68(s, 2H), 7.67(s, 2H), 4.80 (br, 2H), 3.73 (m, 4H), 2.21 (m, 2H), 1.87 (m, 4H), 1.32 (m, 4H), 1.06 (d, 6H), 0.80 (d, 6H).
5b₉	8.89(s, 2H), 7.62(s, 2H), 7.58(s, 2H), 4.80(q, 2H), 3.81(t, 4H), 1.86(m, 4H), 2.24(m, 2H), 1.32-1.39(m, 10H), 1.01 (d, 6H), 0.85 (d, 6H).

¹H NMR spectra were taken in D₂O (**5**), using TMS as internal standard.

TABLE-3
¹³C NMR SPECTRA OF COMPOUNDS **5**

Compound	¹³ C NMR, δ (ppm)
5a₂	14.6, 25.4, 58.6, 122.4, 123.6, 138.7, 172.2
5a₃	14.8, 25.2, 34.8, 58.9, 122.3, 123.4, 137.4, 172.2
5a₄	14.8, 25.6, 38.6, 64.6, 122.8, 123.0, 137.4, 172.2
5a₆	15.0, 27.3, 30.3, 54.8, 72.4, 122.8, 123.6, 137.3, 172.2
5a₉	15.1, 26.3, 28.3, 30.4, 32.5, 54.8, 72.2, 122.7, 123.6, 137.2, 172.1
5b₂	17.3, 25.3, 28.9, 53.1, 70.7, 122.4, 123.5, 138.7, 172.2
5b₃	17.4, 25.2, 28.3, 52.3, 71.7, 122.3, 123.4, 137.4, 172.2
5b₄	17.9, 25.3, 30.4, 52.1, 72.5, 122.5, 123.7, 137.4, 172.1
5b₆	18.2, 25.2, 27.6, 30.5, 55.0, 73.2, 120.3, 123.4, 137.0, 172.2
5b₉	17.8, 25.2, 26.1, 28.3, 30.0, 32.5, 52.5, 70.2, 122.3, 123.5, 137.1, 172.3

geminal dicationic ionic liquid in different solvent were investigated (Table-4). It was found that all the chiral *geminal* dicationic ionic liquid synthesized were dissolved in water and methanol and insoluble in ethyl acetate, acetone, chloroform, which is quite similar to the monocationic ionic liquids with Br⁻ as anion.

Conclusion

A synthetic route toward a novel chiral *geminal* dicationic ionic liquid from amino acids has been described. The solubility and other physical properties have been preliminary studied, further investigations for their application is under way.

ACKNOWLEDGEMENTS

This work is supported by the Construct Program of the Key Discipline in Hunan Province (2012) and Aid Program for Science and Technology Innovative Research Team in Higher Educational Institutions of Hunan Province (2012-318) and

TABLE-4
SOLUBILITIES OF THE CHIRAL GEMINAL
DICATIONIC IONIC LIQUID

Chiral geminal dicationic ionic liquid	Solubility				
	Water	Methanol	Ethyl acetate	Acetone	Chloroform
5a₂	s	s	ins	ins	ins
5a₃	s	s	ins	ins	ins
5a₄	s	s	ins	ins	ins
5a₆	s	s	ins	ins	ins
5a₉	s	s	ins	ins	ins
5b₂	s	s	ins	ins	ins
5b₃	s	s	ins	ins	ins
5b₄	s	s	ins	ins	ins
5b₆	s	s	ins	ins	ins
5b₉	s	s	ins	ins	ins

^as = soluble, ins = insoluble.

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Science and Technology Planning Project of Hunan Province (no. 2013FJ3004) and the Key Scientific Research Project of the Hunan Provincial Education Department (Grant No. 2013A).