ISSN 1070-3632, Russian Journal of General Chemistry, 2014, Vol. 84, No. 7, pp. 1302–1307. © Pleiades Publishing, Ltd., 2014.
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Stereoselective Oxidation of Methyl Phenyl Sulfide in the Presence of Chiral Ionic Liquids

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Received December 16, 2013

Abstract—Several ionic liquids containing a chiral center either in the cation or in the anion have been prepared. They have been applied as catalysts and solvents for stereoselective oxidation of methyl phenyl sulfide to obtain the respective sulfoxide.

Keywords: ionic liquid, oxidation, chirality, sulfide
DOI: 10.1134/S1070363214070093

Development of efficient and environmentally friendly oxidants of organic sulfides and disulfides is a topical task, as the so obtained products (sulfoxides, sulfones, and thiosulfonates) may act as promising complexing agents, surfactants, plant growth factors, and drugs. Many of the biologically active compounds contain a chiral sulfinyl group; hence, catalytic systems allowing for asymmetric oxidation of sulfides into sulfoxides with high enantioselectivity are on demand. The application of ionic liquids for chiral oxidation of sulfur-containing substrates has been reported in [1]. Nowadays, conventional Bolm and Kagan catalytic systems are widely used; however, such methods are not universal, and they are technologically sophisticated [2–6].

In this work we studied asymmetric oxidation of organic sulfide in the presence of chiral ionic liquids containing an asymmetric center either in the cation or in the anion. Being the chirality source, they were used as oxidant or as solvent. In the literature, there have been published examples of asymmetric sulfides oxidations where the same molecule acted both as oxidant and as asymmetric center [7, 8].

To be used in asymmetric oxidation of sulfides, a ionic liquid with a chiral center in the anion should be easily prepared; it should possess a low melting point (sulfoxides racemization is substantially accelerated above room temperature); it should contain functional groups participating in the oxidation process; the racemization should be avoided at any stage of the ionic liquid preparation.

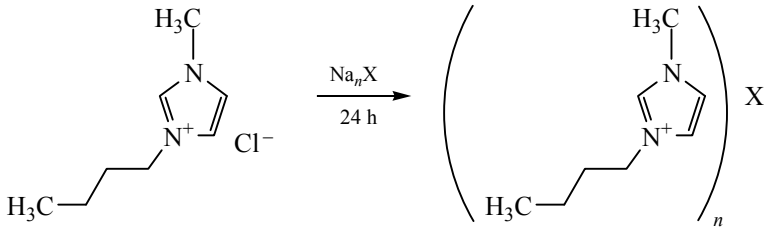
Taking into account the above-listed considerations, in this work we used imidazolinium salts of organic acids prepared via the ion exchange. Many of such salts are liquid at room temperature; containing carboxylic groups, they can be converted into the peracid salts under conditions of the oxidation, they can then act as an oxidant bearing an asymmetric center. The following acids were used for the ionic liquids preparation: L-serine, L-lactic acid, and L-tartaric acid (they are commercially available in the enantiopure form).

The following oxidants were used: *tert*-butyl hydroperoxide, cumene hydroperoxide, hydrogen peroxide (30 wt % aqueous solution), hydrogen peroxide–urea complex, and benzoyl peroxide. Ionic liquids **Ia–Ic** containing chiral center in the anion were prepared via ion exchange between 1-butyl-3-methylimidazolinium chloride and sodium salts of L-lactic acid, L-tartaric acid, and L-serine (Scheme 1).

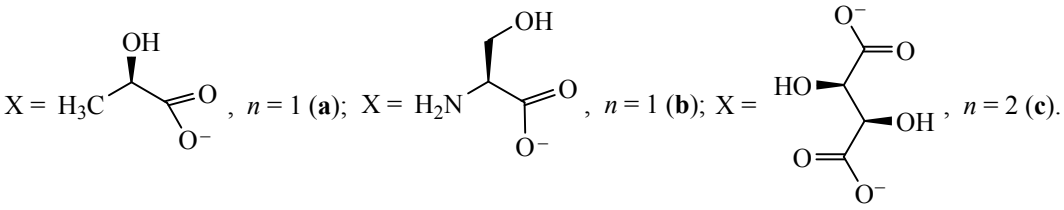
Ionic liquids containing chiral center in the cation were prepared starting from commercially available asymmetric natural alcohols: L-menthol and L-borneol (**IIa, IIb**) [9] (Scheme 2).

Firstly, ester of chloroacetic acid and the corresponding alcohol was prepared; the second stage was 1-methylimidazole alkylation with the so prepared

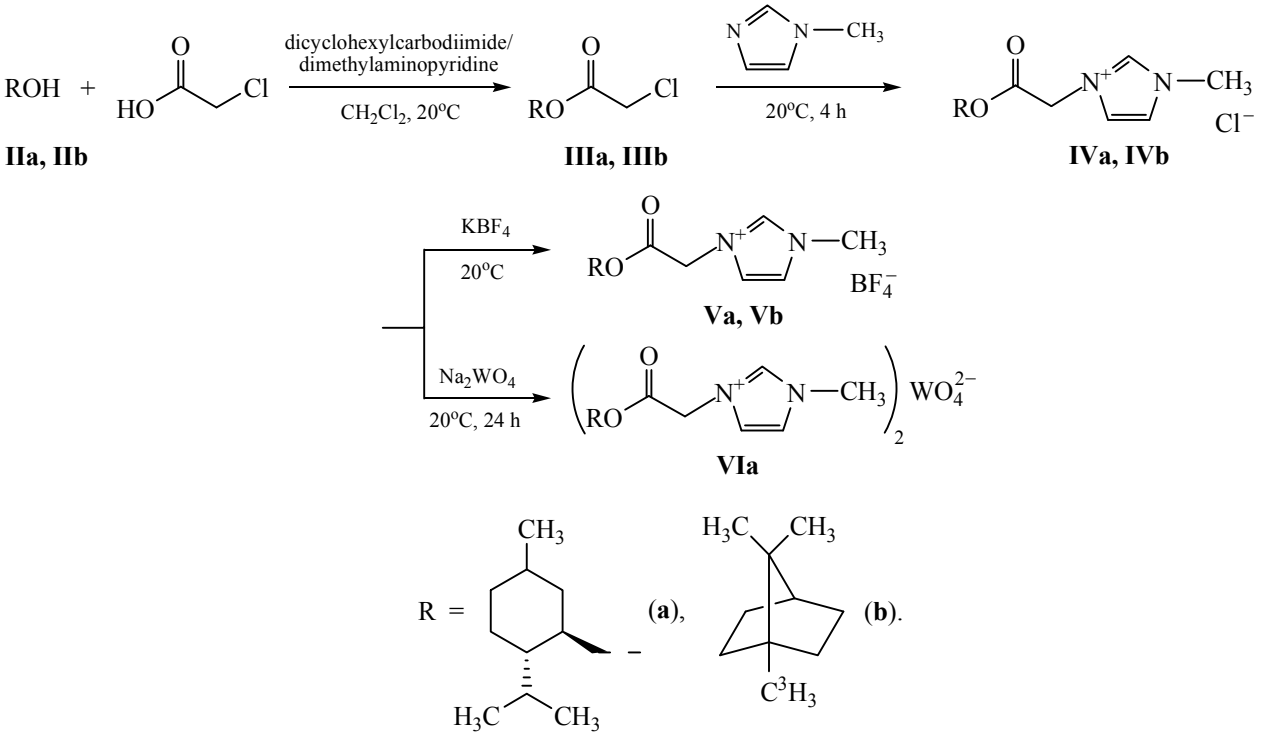
Scheme 1.



Ia–Ic



Scheme 2.



IIa, IIb **IIIa, IIIb** **IVa, IVb**

Va, Vb

VIa

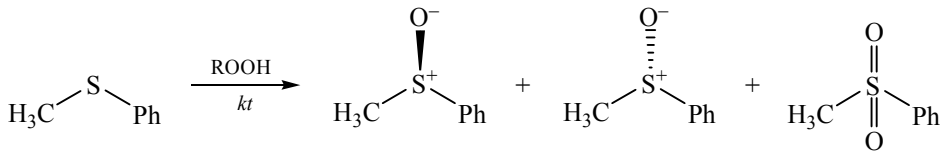
esters. The reaction yields were 82% (menthol) and 56% (borneol). The second stage implied ion exchange between the prepared ionic liquids and potassium tetrafluoroborate.

Following the scheme, we obtained tetrafluoroborate of the menthol derivative (yellow oil) with the yield of 77%; in the case of borneol, yield of the product (brown oil) was 92%.

To prepare ionic liquid containing tungstate anion we performed ion exchange of the menthol derivative chloride with sodium tungstate.

Mass spectrometry (inductively coupled plasma) revealed 7 mg of tungsten in 1 mL of 2 wt % aqueous solution of the ionic liquid; that corresponded to the 2 : 1 complex composition and evidenced the completeness of anion exchange reaction.

Scheme 3.



Oxidation of the model substrate, methyl phenyl sulfide, was performed using the ionic liquid with chiral center in the anion, allowing for high enantiomeric excess at substantial yield of the sulfoxide (up to 80%) [1]. The following oxidants were used: hydrogen peroxide–urea complex, aqueous hydrogen peroxide (37 wt %), 3-chloro-perbenzoic acid, and benzoyl peroxide (Scheme 3). The results obtained under varied conditions are shown in the table.

The oxidation practically did not occur when hydrogen peroxide–urea was used as oxidant (the sulfoxide yield was below 1%).

Addition of 1 mol % of sodium tungstate as co-catalyst increased the sulfoxide yield up to 13%, other conditions being the same. Running the oxidation during 24 h instead of 3 h further increased the sulfoxide yield up to 80%; however, still longer run did not lead to higher sulfoxide yield. The highest yield of the sulfoxide (90%) was achieved using benzoyl peroxide as oxidant and sodium tungstate as co-catalyst. The oxidant and methyl phenyl sulfide were readily soluble in the ionic liquids, and 24 h stirring at room temperature in all cases gave more than 60% of methyl phenyl sulfoxide.

Ionic liquids with chiral center in the cation containing metal atom in the anion (for example, tungstate ion) act as oxidation catalysts in nonpolar medium, under conditions of contact ion pairs formation. Even though there are examples of using ionic liquids as catalyst of asymmetric sulfide oxidation [1], in all the reported cases the asymmetric center was in the anion of the ionic liquid. We attempted comparative study of methyl phenyl sulfoxide oxidation using the above-mentioned ionic liquids with chiral center in the cation and 3-chloroperbenzoic acid as oxidant; however, the results were poor (the sulfoxide yield was below 5%). Variation of the oxidant and the reaction duration did not improve the sulfoxide yield.

The enantiomeric composition of the oxidation products was analyzed in the cases of reactions with the sulfoxide yield above 50%. In all cases the enantiomeric excess did not exceed 10%; the best result (*ee* 10%) was achieved when ionic liquid Ia was used as solvent (see table).

Oxidation of methyl phenyl sulfide under conditions of the modified Sharpless reaction [diethyl tartrate being substituted with 1-butyl-3-methylimidazolinium (*R,R*)-tartrate] allowed for the increased methyl phenyl sulfoxide yield of 87%, the enantiomeric excess being of 79% (HPLC).

To conclude, in this work we prepared a number of ionic liquids, and they were used in model reaction of methyl phenyl sulfide oxidation. So far we were not able to achieve high enantiomeric excess of the product by using the ionic liquids as chiral solvent. Using ionic liquids in conventional systems of asymmetric oxidation of sulfides was successful and helped improving the sulfoxide yield. The properties of ionic liquids like easy preparation, excellent solubility in most of organic solvents, etc may further extend the possibilities of the developed synthetic methods by substitution of conventional chirality sources with the chiral ionic liquids.

EXPERIMENTAL

The starting chemicals and solvents used in this work were commercially available products (Reakhim, Aldrich, and Acros Organic). The solvents were purified by distillation using standard methods [10].

^{1}H NMR spectra were recorded with the Bruker Avance 400 spectrometer at 400 MHz. 2 wt % solutions in $CDCl_3$ or DMSO-d_6 were studied. Chemical shifts were referenced to internal hexamethyldisiloxane.

Electrospray ionization mass spectra (ESI-MS) were recorded with the AB Sciex QTRAP 3200 instrument (cations registration mode). The samples were prepared in the form of 2 wt % solution in methylene chloride or in water (LS MS Grade Aldrich). Other conditions were as follows: direct input with a syringe, source voltage 5.5 kV, source temperature 300°C, mass range 100–500 Da.

Oxidation of methyl phenyl sulfide with various oxidants in the presence of ionic liquids at 25°C

Comp. no.	Co-catalyst	Reaction time, h	Oxidant	Solvent	Yield of sulfoxide/*ee*, %
Ia	-	3	Hydrogen peroxide–urea	CH_2Cl_2/ 2 wt % EtOH	1/–
Ib					
Ic					
Ia	Na_2WO_4	24			13/–
Ia					80/4
Ib					78/5
Ic					82/5
Ia	Na_2WO_4	24	Benzoyl peroxide	CH_2Cl_2/ 2 wt % EtOH	90/6
Ia	-			-	65/10
Ib	-				61/8
Ic	-				68/8
Ia	Na_2WO_4		*m*-Chloroperbenzoic acid	CH_2Cl_2/ 2 wt % EtOH	54/6
Ia			30% Hydrogen peroxide	CH_2Cl_2/ 2 wt % EtOH	75/5
Ia		48	Hydrogen peroxide–urea	CH_3CN	55/3

The products composition and purity were monitored by gas-liquid chromatography (Kristall-2000M chromatograph with flame ionization detector, Zebron column (l = 30 m, d = 0.32 mm), ZB-1 as liquid phase, temperature ramp 100 to 230°C (sulfides analysis).

Tungsten content was determined by mass spectrometry with inductively coupled plasma (the Agilent 7500c instrument, generator power 1500 W, the rate of plasma forming gas 15 L/min, sample rate 1.15 L/min, resolution 0.7 a. w. u., pressure without plasma 4×10^{-5} Torr, pressure with plasma 4×10^{-4} Torr, measurement time 0.05–0.1 s per point, 3 points per peak, 3 replicates, ^{182}W and ^{184}W isotopes were used).

Calibration was run using the ICP-MS-68 multielement reference, solution B containing 10 mg/L of tungsten. Calibration plots were obtained via successive dilution of the stock solution with 1 wt % aqueous HNO_3 to concentration of 1, 10, and 100 μg/L. The background signal was measured using 1 vol % aqueous HNO_3 (Merck, Germany). For the measurement, a sample to be analyzed was diluted to 1 : 50 and 1 : 1000, and then the signal was measured.

TLC analysis was performed using the Silufol UV 254 or cellulose plates. Depending of the reaction mixture composition, eluents of various polarity were used. The plates were developed in iodine vapor, with UV irradiation, or with potassium permanganate solution.

Enantiomeric excess was determined by means of HPLC using the chiral column with Kromacil 3-Cellucoat CT8032 as the stationary phase; the Shimadzu 231 chromatograph with spectrophotometric detector, λ = 220 nm; hexane–isopropyl alcohol, 40 : 1, as eluent; P = 1 MPa.

1-Butyl-3-methylimidazolium lactate (Ia) [11]. Sodium L-lactate (1.23 g, 11 mmol) was added to solution of 1-methyl-3-butylimidazolium chloride (1.91 g, 11 mmol) in anhydrous acetone (10 mL) at room temperature. After 24 h stirring, the reaction mixture was filtered through porous glass filter with 1 cm layer of zeolite. The solvent was removed, and the residue was dried in a vacuum (2 mmHg) during 24 h. Yield 1.30 g (52%), yellow liquid. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 0.81 t (3H, J 7.3 Hz), 1.19 m (2H), 1.71 m (2H), 3.59 m (1H), 3.87 s (3H),

4.02 m (3H), 4.18 t (2H, *J* 7.1 Hz), 7.80 s (1H), 7.88 s (1H), 9.63 s (1H). Mass spectrum: *m*/*z* 140 [*M* − lactate]$^+$.

1-Butyl-3-methylimidazolium 2-amino-3-hydroxypropionate (Ib) [11]. Sodium salt of L serine (1.21 g, 9.5 mmol) was added at room temperature to solution of 1-methyl-3-butylimidazoluim chloride (1.65 g, 9.5 mmol) in 50 mL of anhydrous acetone, and the mixture was stirred during 24 h. Then the reaction mixture was filtered through a filter with a zeolite layer, and the solvent was distilled off. Yield 1.90 g (83%). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 0.86 t (3H, *J* 7.5 Hz), 1.23 m (3H), 1.74 m (2H), 3.33, 3.47 m (2H), 3.79 m (1H), 3.87 s (3H), 4.18 t (2H, *J* 7.2 Hz), 7.77 s (1H), 7.84 s (1H), 9.36 s (1H). Mass spectrum: *m*/*z* 140 [M_{cation}]$^+$.

1-Butyl-3-methylimidazolium (*R*,*R*)-tartrate (Ic) [11]. 1.82 g (2 eq.) of sodium hydroxide was added to solution of 3.42 g (23 mmol) of tartaric acid in 30 mL of water; the solution was stirred during 30 min, and then concentrated by solvent evaporation. Then the so prepared solution of sodium (*R*,*R*)-tartrate was added to the solution of 1-methyl-3-butylimidazolium chloride (10.00 g, 46 mmol) in 100 mL of anhydrous acetone, and the mixture was stirred at room temperature during 24 h. The solution was evaporated to dryness, 50 mL of CH_2Cl_2 was added; the organic fraction was separated, washed with water (2 × 20 mL), and dried over Na_2SO_4. The solvent was then removed, and the residue was dried in vacuum. Yield 8.10 g (83%), viscous yellow liquid. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 0.86 t (6H, *J* 7.3 Hz), 1.21 m (4H), 1.74 m (2H), 3.40 s (2H), 3.85 s (6H), 4.18 m (2H), 7.75 s (2H), 7.83 s (2H), 9.31 s (2H). Mass spectrum: *m*/*z* 140 [M_{cation}]$^+$.

(1*R*,2*S*)-5-Methyl-2-(propan-2-yl)cyclohexylchloroacetate (IIIa) [9]. Chloroacetic acid (2.35 g, 25 mmol), dicyclohexylcarbodiimide (5.16 g, 25 mmol), and dimethylaminopyridine (0.23 g, 1.9 mmol) were added at 0ºC upon stirring to solution of L-menthol (3.00 g, 19 mmol) in anhydrous CH_2Cl_2 (15 mL). The mixture was stirred during 12 h at room temperature. The suspension was filtered, and the residual was washed with anhydrous CH_2Cl_2 (10 mL). The organic phase was washed with 10 wt % HCl (10 mL), then with saturated $NaHCO_3$ solution (10 mL), and with saturated NaCl solution (10 mL). The product was dried with Na_2SO_4, filtered, and the solvent was distilled off. Yield 2.22 g (50%), yellow oil. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 0.72 d (3H, *J* 7.0 Hz), 0.81 m (1H), 0.85 t (6H, *J* 6.7 Hz), 0.98 m (2H), 1.36 m (2H), 1.62 m (2H), 1.81 m (1H), 1.95 m (1H), 3.98 m (2H), 4.70 m (1H).

1,7,7-Trimethylbicyclo[2.2.1]hept-2-ylchloroacetate (IIIb) [9]. Chloroacetic acid (1.58 g, 20 mmol), dicyclohexylcarbodiimide (5.16 g, 20 mmol), and dimethylaminopyridine (0.23 g, 1 mmol) were added at 0ºC upon stirring to solution of L-borneol (2.00 g, 20 mmol) in anhydrous CH_2Cl_2 (15 mL). The mixture was stirred during 12 h at room temperature. The suspension was filtered, and the residue was washed with anhydrous CH_2Cl_2 (10 mL). The organic phase was washed with 10 wt % HCl (10 mL), then with saturated $NaHCO_3$ solution (10 mL), and with saturated NaCl solution (10 mL). The product was dried with Na_2SO_4, filtered, and the solvent was distilled off. Yield 1.66 g (36%), dark-yellow oil. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 0.76 s (3H), 0.80 d (6H, *J* 11.0 Hz), 0.94 m (1H), 1.15 m (2H), 1.65 m (2H), 1.86 m (1H), 2.24 m (1H), 4.35 d (2H, *J* 3.7 Hz), 4.85 m (1H).

1-Methyl-3-[(1*R*,2*S*)-5-methyl-2-(prop-2-yl)cyclohexyloxycarbonylmethyl]-1*H*-imidazol-3-ium chloride (IVa) [9]. 0.78 g (1 equiv.) of 1-methylimidazole was added to ester **IIIa** (2.22 g, 9.5 mmol); the solution was stirred during 4 h at 80°C. After that, the formed solid white substance was washed with benzene (2 × 10 mL), filtered, and dried in a vacuum. Yield 2.48 g (82%), dark-yellow powder, mp 72–73°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 0.70 d (3H, *J* 6.9 Hz), 0.81 m (1H), 0.86 t (6H, *J* 6.9 Hz), 0.99 m (2H), 1.33 m (2H), 1.61 m (2H), 1.83 m (1H), 1.99 m (1H), 3.90 s (3H), 4.66 m (1H), 5.19 m (2H), 7.75 m (2H), 9.18 s (1H).

1-Methyl-3-{(1,7,7-trimethylbicyclo[2.2.1]-hept-2-yl)oxycarbonylmethyl}-1*H*-imidazol-3-ium chloride (IVb) [9]. 0.43 g (1 equiv.) of 1-methylimidazole was added to ester **IIIb** (1.20 g, 5.2 mmol); the solution was stirred during 4 h at 80°C. After that, the formed brown oil was washed with benzene (3 × 10 mL) and dried in a vacuum. Yield 0.91 g (56%). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 0.76 s (3H), 0.80 d (6H, *J* 7.2 Hz), 0.94 m (1H), 1.09 m (2H), 1.63 m (3H), 1.86 m (1H), 2.20 m (1H), 3.86 s (3H), 4.83 m (1H), 5.25 m (2H), 7.72 m (2H), 9.15 s (1H).

1-Methyl-3-[(1*R*,2*S*)-5-methyl-2-(prop-2-yl)cyclohexyloxycarbonylmethyl]-1*H*-imidazol-3-ium tetrafluoroborate (Va) [9]. 0.88 g (1 equiv.) of KBF_4 was added to a solution of 2.22 g (7 mmol) of compound

IVa in 10 mL of water, and the mixture was stirred during 5 h at room temperature. After that, water was distilled off; CH_2Cl_2 was added to the residue; the mixture was filtered through zeolite layer; the filtrate was dried over Na_2SO_4; the solvent was distilled off; and the residue was dried in a vacuum. Yield 2.00 g (77%), pale-yellow powder, mp 37–38°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 0.70 d (3H, *J* 7.1 Hz), 0.81 m (1H), 0.86 t (6H, *J* 7.1 Hz), 0.99 m (2H), 1.33 m (2H), 1.61 m (2H), 1.83 m (1H), 1.99 m (1H), 3.90 s (3H), 4.66 m (1H), 5.19 m (2H), 7.72 m (2H), 9.14 s (1H). Mass spectrum: *m*/*z* 280 $[M - BF_4]^+$.

1-Methyl-3-{(1,7,7-trimethylbicyclo[2.2.1]hept-2-yl)oxycarbonylmethyl}-1*H*-imidazol-3-ium tetrafluoroborate (Vb) [9]. 0.37 g (1 equiv.) of KBF_4 was added to a solution of 0.91 g (2.9 mmol) of compound **IVb** in 10 mL of water, and the mixture was stirred during 48 h at room temperature. After that, water was distilled off; CH_2Cl_2 was added to the residue; the mixture was filtered through zeolite layer; the filtrate was dried over Na_2SO_4; the solvent was distilled off; and the residue was dried in a vacuum. Yield 0.87 g (92%), brown oil. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 0.76 s (3H), 0.80 d (6H, *J* 7.3 Hz), 0.94 m (1H), 1.09 m (2H), 1.63 m (3H), 1.86 m (1H), 2.20 m (1H), 3.86 s (3H), 4.83 m (1H), 5.25 m (2H), 7.69 m (2H), 9.10 s (1H). Mass spectrum: *m*/*z* 278 $[M - BF_4]^+$.

1-Methyl-3-[(1*R*,2*S*)-5-methyl-2-(prop-2-yl)cyclohexyloxycarbonylmethyl]-1*H*-imidazol-3-ium tungstate (VIa) [9]. 10.56 g (32 mmol) of $Na_2WO_4{\cdot}2H_2O$ was added to a solution of 20.00 g (64 mmol) of compound **IVa** in 100 mL of water, and the mixture was stirred during 24 h at room temperature. After that, water was distilled off; CH_2Cl_2 was added to the residue; the mixture was filtered through zeolite layer; the filtrate was dried over Na_2SO_4; the solvent was distilled off; the residue was dried in a vacuum. Yield 10.87 g (42%), yellow-green oil. ^{1}H NMR spectrum (DMSO-d_6, 400 MHz), δ, ppm: 0.68 d (3H, *J* 7.0 Hz), 0.81 m (1H), 0.86 t (6H, *J* 6.9 Hz), 0.99 m (2H), 1.33 m (2H), 1.61 m (2H), 1.83 m (1H), 1.91 m (1H), 3.89 s (3H), 4.63 m (1H), 5.24 m (2H), 7.72 m (2H), 9.12 s (1H). Mass spectrum: *m*/*z* 280 $[M - BF_4]^+$.

Methyl phenyl sulfide oxidation [1]. Methyl phenyl sulfide (0.20 g, 1.6 mmol), 1 mol % of the chiral ionic liquid and 1.15 equiv. of the oxidant (hydrogen peroxide–urea, 30 wt % hydrogen peroxide solution, 3-chloroperbenzoic acid, or benzoyl peroxide) were added to 5 mL of the solvent (CH_2Cl_2–C_2H_5OH 50 : 1 or CH_3CN). The mixture was stirred at room temperature during 3–48 h. The mixture was decanted or filtered, washed with water, and analyzed.

Methyl phenyl sulfide oxidation in the Kagan system [2]. Titanium tetraisopropylate (0.14 mg, 0.5 mmol) and the ionic liquid **Ic** (0.42 g, 1 mmol) were dissolved in 5 mL of anhydrous CH_2Cl_2 Under argon. 9 μL of water were added dropwise through the septum. The reaction mixture was stirred during 30 min till homogenization; and methyl phenyl sulfide (0.062 g, 0.5 mmol) was added. The solution was cooled to –20°C, and 200 μL (1 mmol) of 5 mol/L solution of *tert*-butyl hydroperoxide was added. The mixture was stirred at –20°C during 12 h. The reaction was then quenched by addition of 2 mL of water; the mixture was filtered, and the organic phase was analyzed.

ACKNOWLEDGMENTS

This work was financially supported by the Russian Foundation for Basic Research (project no. 12-03-00260).

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