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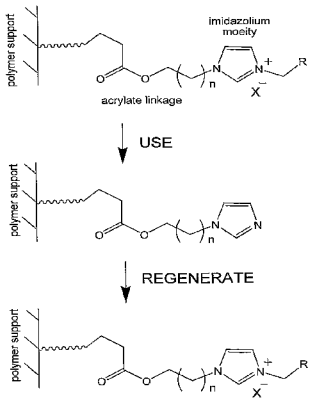

FIGURE 1

(57) Abstract: The present invention relates to novel imidazolium compounds and improved method for the preparation of imidazolium salts. More specifically the invention describes preparation of 1,3-substituted imidazolium reagents whereby the reactive species can be regenerated upon consumption and readily re-usable for versatile chemical transformations. The syntheses of novel imidazolium salts are for applications as oxidizing agent in environmentally electrochemical reactions, internal electrolyte for durable reference electrode and lipophilic salts for anion chemical sensors.

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METHOD FOR PREPARATION OF REGENERATIVE IMIDAZOLIUM REAGENTS

FIELD OF INVENTION

This invention relates to method for the preparation of novel imidazolium reagents. More specifically the invention describes preparation of 1,3-substituted imidazolium reagents whereby the reactive species can be regenerated upon consumption and readily re-usable for versatile chemical transformations.

BACKGROUND OF THE INVENTION

The US 5,969,150 disclosed that the present invention relates to novel imidazolium compounds and improved processes for the preparation of imidazolium cations with one or more imidazolium moieties optionally substituted with the same or different substituents, which are prepared from a reactant with at least one N--C--C--N group, by reacting with with an N-substituted or N,N-disubstituted thioformamide, formamide acetal or thioformamide acetal, in the presence of a halogenating agent. Examples of suitable halogenating agents include but are not limited to thionyl chloride, phosgene, and phosgene derivatives. Reactants containing more than one additional N--C--C--N group may also be used to prepare compounds with two or more imidazolium groups, by the procedures of the present invention. Certain compounds of the invention prepared from reactants with multiple N--C--C--N groups may have both unreacted N--C--C--N moieties and substituted imidazolium groups.

In another US granted patent, US 5,817,823 disclosed that the present invention is a method of preparing 2-substituted imidazoles from readily available imidazoles having a leaving group in the 2-position, by alkylating the imidazole under mild conditions to afford a 3-N-alkylated imidazolium salt; and

coupling the imidazolium salt with a nucleophile also under mild conditions to afford a 2-substituted 3-N-alkylated imidazolium salt. The reaction product can optionally be isolated and purified. The 2-substituted 3-N-alkylated imidazolium salt is hydrolyzed to afford a 2-substituted imidazole. Alternatively, the imidazole is coupled with a nucleophile in the presence of fluoride ion to provide a 2-substituted imidazole.

The present invention addresses preparation and applications of imidazolium reagents in environmentally friendly manner. In particular the reagents are intended for use as reactant for halogenation of metals. Although procedures for halogenation of metals have been described previously, these methods often utilize or release flammable or toxic gases by-products. Similarly, methods related to the process of synthesizing imidazolium salts and imidazole derivatives as described in the prior arts use or produce toxic chemicals and gases such as phosgene and chlorine gases.

Hence there is still a need in the art for a process for synthesizing imidazolium reagents using safe preparation methods and employ it for environmentally friendly or green chemical or electrochemical transformations. We are developing novel electrochemical process whereby the by-products are non-toxic and free from emission of green-house gases. Moreover, the reagents can be re-used and the by-products can be re-covered for preparative use.

SUMMARY OF THE INVENTION

The present invention describes preparation of 1,3-substituted imidazolium reagents, whereby the hydroxyl substituent at N1 can be converted to acrylate group and polymerized to solid-support matrix backbone or remains free for dissolution in aqueous or polar organic solvents such as dimethylsulfoxide,

dioxane, terahydrofuran or alcohols or mixture of solvents. In a chemical or electrochemical transformation the substituent at N1 breaks away to form a stable organic reactive intermediate and an aromatic heterocycle is formed. The substituent at N1 can be reintroduced quickly and efficiently to regenerate the imidazolium reagent. Halogenation of metals can be achieved in this fashion thus avoiding the use of toxic chemicals or release of flammable gases. The present invention can also be used as organic chloride internal reference electrolyte for reference electrode, internal solution for chemical sensors, lipophilic salts for chemical sensors and versatile reagent for a wide range of organic transformations.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig.1 illustrates an exemplified diagram of a polymer-bound regenerative imidazolium reagent.

Fig. 2 illustrates an exemplified diagram of free hydrophilic regenerative imidazolium reagent.

DETAILED DESCRPTION OF THE PREFERRED EMBODIMENT

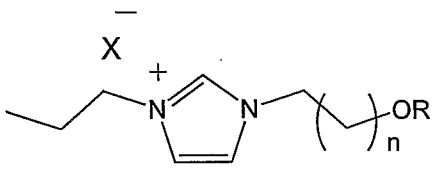
The application of regenerative imidazolium reagent, polymer-bound to a solid support as illustrated in Figure 1. In this embodiment the imidazolium moiety is polymerized onto the matrix backbone and the pendant cationic species releases a stable organic reactive species and generate a pendant aromatic heterocycle. The substituent at N1 of the imidazolium moiety is transferred during a chemical or electrochemical transformation to produce an imidazole pendant group. Upon consumption of the reactive reagent, the substituent at N1 can be reintroduced using a chemical transformation to get back the imidazolium moiety and thus reactivate the reagent.

In another embodiment the imidazolium reagents present in its un-protected hydrophilic hydroxyl (alcohol) form, dissolved in water or polar solvents. Upon application in a chemical transformation, the reactive moiety releases a stable organic reactive species and generates a pendant aromatic heterocycle. The imidazolium reagent can be regenerated quickly and efficiently by re-introducing the reactive species at N1.

Figure 2 illustrates the application of free hydrophilic regenerative imidazolium reagent in aqueous or polar organic solvents such as dimethylsulfoxide, dioxane, tetrahydrofuran or alcohols.

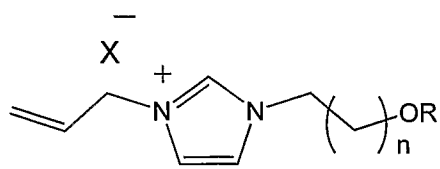
For our efforts in developing improved chemical sensors, imidazolium salts have great potential in the following areas; as oxidizing agents in electrochemical transformations; as electrolyte for reference electrode; as lipophilic salts for anion chemical sensors and as electrolyte in internal layer of anion chemical sensor.

The imidazolium oxidizing agents is an environmentally friendly reagents and support green electrochemical transformations i.e. redox reactions. The novel electrochemical process produces by-products that are non-toxic and free from emission of green-house gases. Moreover, the reagents can be re-used and the by-products can be re-covered for preparative use. The deployment of sensor system requires the use of maintenance-free reference electrode with minimal loss of chloride ion internal electrolyte. Use of Imidazolium chloride having polymerizable moiety is a good solution to prevent loss of chloride internal reference electrolyte in silver-silver chloride reference electrode.



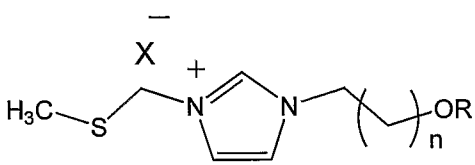
2

R = H, CH_3, Ts, $COCH=CH_2$
X = Cl, Br, I, F, OAc, BF_4, PF_6
n = 0, 1, 2, 3, 4, 5



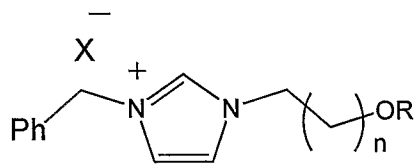
3

R = H, CH_3, Ts, $COCH=CH_2$
X = Cl, Br, I, F, OAc, BF_4, PF_6
n = 0, 1, 2, 3, 4, 5



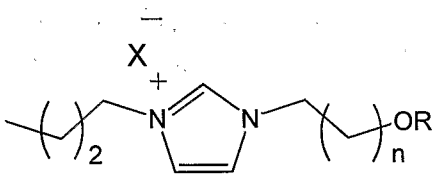
4

R = H, CH_3, Ts, $COCH=CH_2$
X = Cl, Br, I, F, OAc, BF_4, PF_6
n = 0, 1, 2, 3, 4, 5



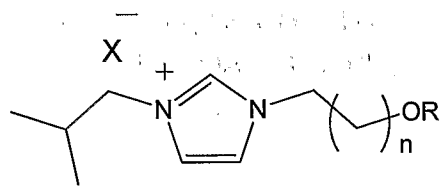
5

R = H, CH_3, Ts, $COCH=CH_2$
X = Cl, Br, I, F, OAc, BF_4, PF_6
n = 0, 1, 2, 3, 4, 5



6

R = H, CH_3, Ts, $COCH=CH_2$
X = Cl, Br, I, F, OAc, BF_4, PF_6
n = 0, 1, 2, 3, 4, 5



7

R = H, CH_3, Ts, $COCH=CH_2$
X = Cl, Br, I, F, OAc, BF_4, PF_6
n = 0, 1, 2, 3, 4, 5

Table 1: The regenerative imidazolium reagents

Referring now to Table 1,each imidazolium salt contains substituent at N_3 that forms delocalized stable radical upon reduction and fragmentation. The imidazole precursor can be recovered for re-use. The radical fragments dimerize to produce volatile hydrocarbons that can be collected as use high purity reagents. The disclosed novel imidazolium salts can be used for applications as oxidizing agent in environmentally electrochemical reactions,

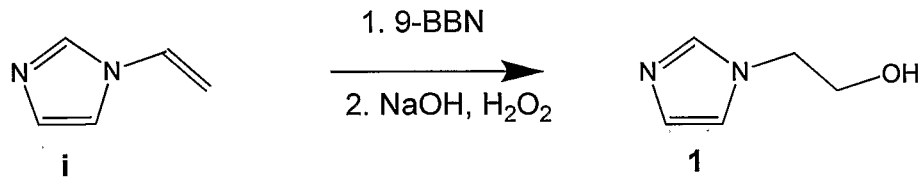
internal electrolyte for durable reference electrode and lipophilic salts for anion chemical sensors.

The present invention may be better understood by reference to the following non-limiting examples, which are provided as exemplary of the invention. The following examples are presented in order to more fully illustrate the preferred embodiments of the invention. They should in no way be construed, however, as limiting the broad scope of the invention.

The regenerative imidazolium reagents **2**, **3**, **4**, **5**, **6** and **7** can be prepared in synthetic transformations as described in the following examples.

Example 1

Preparation of 1-Ethanol Imidazole (1)



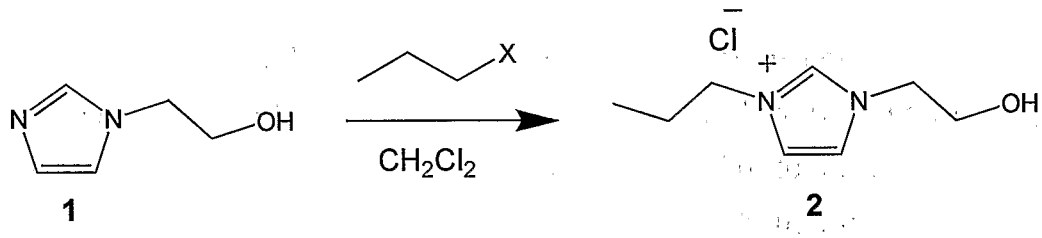
i 1

A 100-mL round-bottom flask, equipped with reflux condenser and magnetic stirrer was flame dried while flushed with nitrogen. Anhydrous tetrahydrofuran (THF) 50 mL was added into the flask via syringe. THF solution of 0.5M 9-borabicyclo[3.3.1]nonane (9-BBN) (0.02 mole) was added, followed by 0.021 mole of freshly distilled 1-vinyl imidazole. The reaction mixture was refluxed for 5 hours. The reaction mixture was gradually cooled to room temperature and 25 mL of 3M odium hydroxide

solution was added. Later 25 mL of 30% hydrogen peroxide was added dropwise into the flask and the mixture was stirred for 5 hours to complete oxidation. The reaction mixture was extracted with 20-mL portions of ethyl ether, and the combined extracts dried with anhydrous magnesium sulfate. Distillation under reduced pressure gave 83% of **1**.

Example 2

Preparation of 3-*n*-Propyl-1-Ethanol Imidazolium Chloride (2) and 3-*n*-Butyl-1-Ethanol Imidazolium Chloride (6)

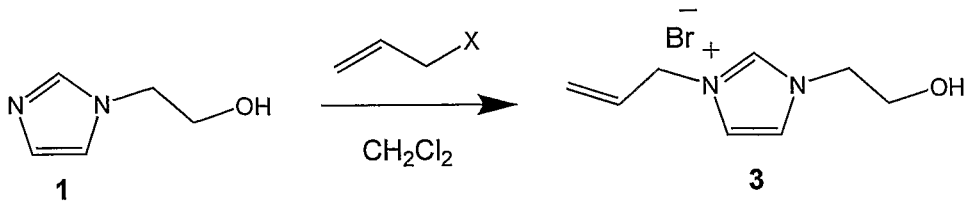


1 **2**

A 50-mL three-necked, round-bottomed flask, equipped with thermometer, nitrogen inlet, addition funnel, magnetic stirrer and reflux condenser was flame dried and flushed with nitrogen. The flask was charged with 25 mL of anhydrous dichloromethane. Freshly distilled 1-ethanol imidazole (**1**, 0.01 mol) was added into the flask. The flask was chilled with ice-water bath and 1-chloropropane (0.011 mol) in 10 mL of anhydrous dichloromethane was added cautiously into the flask with continous stirring over 20 minutes. The solution was heated under reflux for 14 hours and then allowed to cool to room temperature. The dichloromethane solvent was removed under vacuum distillation through Vigreaux column to give 81% of imidazolium chloride **2**. *n*-Butyl-1-ethanol imidazolium chloride (**6**) can be prepared following this procedure from 1-chlorobutane.

Example 3

Preparation of 2-Propenyl-1-Ethanol Imidazolium Bromide (3)

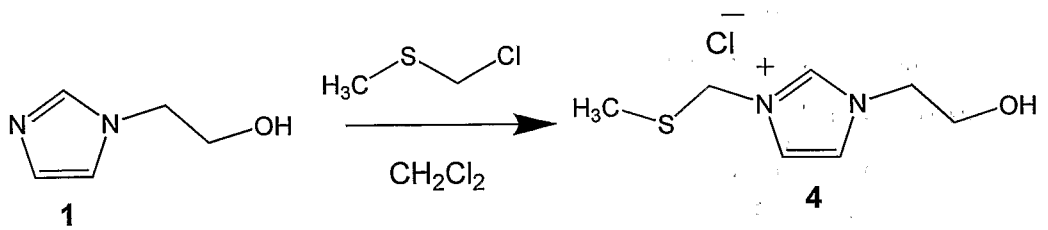


1 3

A 50-mL three-necked, round-bottomed flask, equipped with thermometer, nitrogen inlet, addition funnel, magnetic stirrer and reflux condenser was flame dried and flushed with nitrogen. The flask was charged with 25 mL of anhydrous dichloromethane. Freshly distilled 1-ethanol imidazole (**1**, 0.01 mol) was added into the flask. The flask was chilled with ice-water bath and 3-bromo-1-propene (0.011 mol) in 15 mL of anhydrous dichloromethane was added cautiously into the flask with continous stirring over 30 minutes. The solution was heated under reflux for 8 hours and then allowed to cool to room temperature. The dichloromethane solvent was distilled under to give 87% of imidazolium bromide **3**.

Example 4

Preparation of 3-Methyl thiomethyl-1-Ethanol Imidazolium Chloride (4)



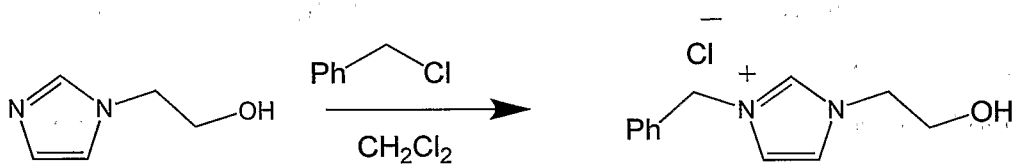
1 4

A 50-mL three-necked, round-bottomed flask, equipped with thermometer, nitrogen inlet, addition funnel, magnetic stirrer and reflux condenser was flame dried and flushed with nitrogen. The flask was charged with 25 mL of anhydrous dichloromethane. Freshly distilled 1-ethanol imidazole (**1**, 0.01

mol) was added into the flask. The flask was chilled with ice-water bath and chloromethyl methyl sulfide (0.011mol) in 15 mL of anhydrous dichloromethane was added cautiously into the flask with continous stirring over 30 minutes. The solution was heated under reflux for 14 hours and then allowed to cool to room temperature. The dichloromethane solvent was distilled under reduced pressure to give 76% of 3-methyl thiomethyl-3-1-ethanol imidazolium chloride **4**.

Example 5

Preparation of 3-Benzyl -1-Ethanol Imidazolium Chloride (5)

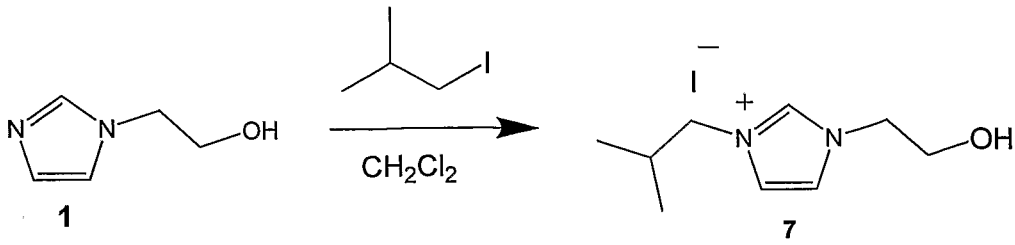


1 **5**

A 50-mL three-necked, round-bottomed flask, equipped with thermometer, nitrogen inlet, addition funnel, magnetic stirrer and reflux condenser was flame dried and flushed with nitrogen. The flask was charged with 25 mL of anhydrous dichloromethane. Freshly distilled 1-ethanol imidazole (**1**, 0.01 mol) was added into the flask. The flask was chilled with ice-water bath and benzyl chloride (0.011 mol) in 15 mL of anhydrous dichloromethane was added cautiously into the flask with continous stirring over 20 minutes. The solution was heated under reflux for 5 hours and then allowed to cool to room temperature. The dichloromethane solvent was distilled under to give 92% of 3-benzyl-1-ethanol imidazolium chloride **5**.

Example 6

Preparation of 3- *iso*-Butyl -1-Ethanol Imidazolium Chloride (7)

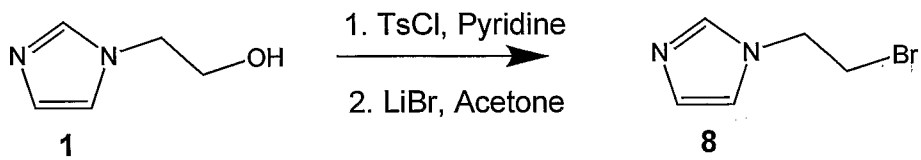


1 7

A 50-mL three-necked, round-bottomed flask, equipped with thermometer, nitrogen inlet, addition funnel, magnetic stirrer and reflux condenser was flame dried and flushed with nitrogen. The flask was charged with 25 mL of anhydrous dichloromethane. Freshly distilled 1-ethanol imidazole (**1**, 0.01 mol) was added into the flask. The flask was chilled with ice-water bath and *iso*-butyl iodide (0.011mol) in 15 mL of anhydrous dichloromethane was added cautiously into the flask with continous stirring over 30 minutes. The solution was heated under reflux for 10 hours and then allowed to cool to room temperature. The dichloromethane solvent was distilled under to give 87% of 3-*iso*-butyl-1-ethanol imidazolium chloride **5**.

Example 7

Preparation of 1-Bromoethyl Imidazole (8)



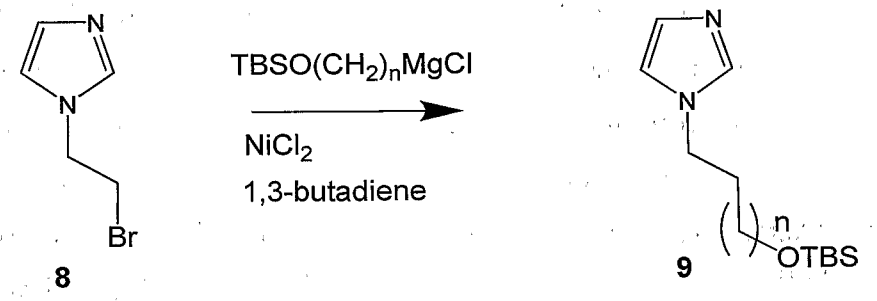
1 8

The hydroxyl group in1-ethanol imidazole (1) was converted to tosylate leaving group following literature procedure with tosyl chloride and anhydrous pyridine. The tosylate leaving group is substituted by bromide in the following procedure.

A 50-mL three-necked, round-bottomed flask, nitrogen inlet, addition funnel, magnetic stirrer and reflux condenser was flame dried and flushed with nitrogen. The flask was charged with 20 mL of freshly distilled acetone. Anhydrous lithium bromide (0.012 mol) was added into the flask and stirred under flow of nitrogen until all the solid disappeared. The flask was chilled with ice-water bath and tosylated 1-ethanol imidazole **1** (0.010 mol) in 15 mL of anhydrous ethyl ether was added cautiously into the flask with continous stirring over 30 minutes. The solution was heated under reflux for 8 hours and then allowed to cool to room temperature. Sodium bicarbonate solution (50 mL) was added into the decanted solution mixture. The organic layer separated and the aqueous layer extracted with 10 mL portion of ethyl ether. The combined organic layers dried and anhydrous magnesium sulfate and the solvent removed under reduced pressure to give 87% of 1-bromoethyl imidazole **8**.

Example 8

Preparation of 1-Hydroxyalkyl (n =4) Imidazole (9)



Silylated 1-hydroxyalkyl imidazole (**9**) can be prepared by coupling of the respective Grignard reagent 1-bromoethyl imidazole (**8**) catalayzed by nickel(II) chloride and 1,3-butadiene. 4-Chloro-1-butanol was extracted with sodium bicarbonate and dried with anhydrous magnesium sulfate and distilled under reduced pressure. Freshly distilled 4-Chloro-1-butanol was silylated using TBSCl in the presence of pyridine following literature procedure. The silylated

chloride was converted to the respective Grignard reagent in refluxing ethyl ether following standard procedure.

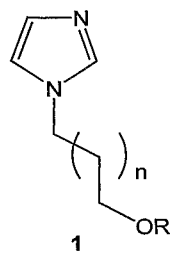
A 50-mL three-necked, round-bottomed flask, nitrogen inlet, addition funnel, magnetic stirrer and reflux condenser was flame dried and flushed with nitrogen. The flask was charged with 25 mL of freshly distilled ethyl ether, anhydrous nickel (II) chloride (0.012 mol). The flask was chilled with dry ice-acetone bath and 1,3-butadiene bubbled into the mixture (0.05 mol). The reaction mixture was stirred for 1 hour until all solid material dissolved and homogenous solution resulted. Solution of the above Grignard reagent from silylated 4-chloro-1-butanol (0.02 mol) in 15 mL of ethyl ether was added dropwise into the mixture. The mixture was stirred for 2 hours before 1-bromoethyl imidazole (0.01 mol) in ethyl ether was added cautiously into the mixture. The solution was stirred for additional 8 hours and then allowed to warm to room temperature. Sodium bicarbonate solution (50 mL) was added into the solution mixture. The organic layer separated and the aqueous layer extracted with 10 mL portion of ethyl ether. The combined organic layers dried and anhydrous magnesium sulfate and the solvent removed under reduced pressure to give 84% of silylated1-hexanol imidazole **9**.

Although the preferred embodiments of the present invention have been described herein, the above descriptions are merely illustrative. Further modification of the invention herein disclosed will occur to those skilled in the respective arts and all such modifications are deemed to be within the scope of the invention as defined by the appended claims.

CLAIMS

1. A method for synthesizing regenerative imidazolium reagents, comprising:
(a) preparing 1-ethanol imidazole (**1**) from 1-vinyl imidazole;
(b) reacting the resulting 1-ethanol imidazole (**1**) or 1-hydroxyalkyl imidazole (**9**) and a primary halide preferably n-propyl halide, n-butyl halide, iso-butyl halide, benzyl halide, allyl halide, wherein the said halides are chloride, bromide and iodide;
(c) exchanging the negatively charged counterions in the resulting imidazolium reagents in claim 1(b) with tetrafluoroborate, acetate, hexafluorophosphate and fluoride;
(d) converting the resulting 1-ethanol imidazole (**1**) in claim 1(a) to a tosylate leaving group;
(e) reacting the resulting product in claim 1(d) with lithium bromide to give the respective 1-bromoethyl imidazole (**8**); and
(f) coupling the resulting 1-bromoethyl imidazole (**8**) in claim 1(e) with silylether Grignard reagent ($TBSO(CH_2)_nMgCl$) in the presence of coupling reagent such as nickel(II) chloride or dilithium tetrachlorocuprate to give the respective 1-hydroxyalkyl imidazoles (**9**).

2. A method of claim 1 characterised in that the step of preparing of 1-ethanol imidazole and its derivatives of formula 1 form 1-vinyl imidazole further

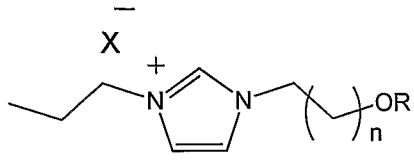


1

R = H, CH_3, Ts, $COCH{=}CH_2$
n = 0, 1, 2, 3, 4

comprising step of; reacting 1-vinyl imidazole and 9-borabicyclo[3.3.1]nonane (9-BBN) in refluxing tetrahydrofuran followed by sodium hydroxide and 30% hydrogen peroxide treatment.

3. A method for preparation of 3-*n*-propyl-1-hydroxyalkyl imidazolium chloride of formula **2** wherein n = 0, 1, 2, 3, 4 or 5



2

R = H, CH_3, Ts, $COCH=CH_2$
X = Cl, Br, I, F, OAc, BF_4, PF_6
n = 0, 1, 2, 3, 4, 5

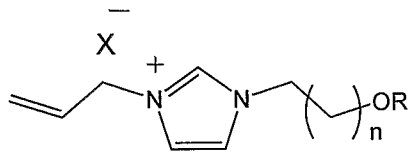
comprising the steps of;

(a) reacting 1-hydroxyalkyl imidazole **1** (n = 0, 1, 2, 3, 4, 5) with 1-chloropropane in refluxing tetrahydrofuran, in anhydrous condition and blanket of argon or nitrogen

(b) converting and protecting the hydroxyl group in **2** to methyl, tosylate or acrylate

(c) exchanging the chloride counterion in **2** to bromide, iodide, fluoride, tetrafluoroborate or hexafluorophosphate

4. A method for preparation of 1-propenyl-3-hydroxyalkyl imidazolium chloride of formula **3** wherein n = 0, 1, 2, 3, 4 or 5



3

R = H, CH_3, Ts, $COCH=CH_2$
X = Cl, Br, I, F, OAc, BF_4, PF_6
n = 0, 1, 2, 3, 4, 5

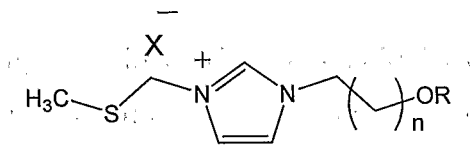
comprising the steps of;

(a) reacting 1-hydroxyalkyl imidazole **1** (n = 0, 1, 2, 3, 4, 5) with 3-bromo-1-propene in refluxing tetrahydrofuran, in anhydrous condition and blanket of argon or nitrogen

(b) converting and protecting the hydroxyl group in **3** to methyl, tosylate or acrylate

(c) exchanging the chloride counterion in **3** to chloride, iodide, fluoride, tetrafluoroborate or hexafluorophosphate

5. A method for preparation of 3-methyl thiomethyl-1-hydroxyalkyl imidazolium chloride of formula **4** wherein n = 0, 1, 2, 3, 4 or 5



4

R = H, CH_3, Ts, $COCH=CH_2$
X = Cl, Br, I, F, OAc, BF_4, PF_6
n = 0, 1, 2, 3, 4, 5

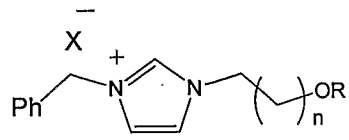
comprising the steps of;

(a) reacting 1-hydroxyalkyl imidazole **1** (n = 0, 1, 2, 3, 4, 5) with chloromethyl methyl sulfide in refluxing tetrahydrofuran, in anhydrous condition and blanket of argon or nitrogen

(b) converting and protecting the hydroxyl group in **4** to methyl, tosylate or acrylate

(c) exchanging the chloride counterion in **4** to chloride, iodide, fluoride, tetrafluoroborate or hexafluorophosphate

6. A method for preparation of 3-benzyl-1-hydroxyalkyl Imidazolium halide of formula **5** wherein n = 0, 1, 2, 3, 4 or 5



5

R = H, CH_3, Ts, $COCH=CH_2$
X = Cl, Br, I, F, OAc, BF_4, PF_6
n = 0, 1, 2, 3, 4, 5

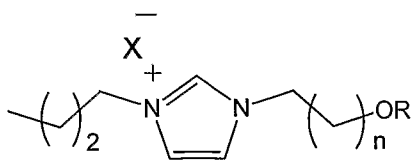
comprising the steps of:

(a) reacting 1-hydroxyalkyl imidazole **1** (n = 0, 1, 2, 3, 4, 5) with benzyl chloride in refluxing tetrahydrofuran, in anhydrous condition and blanket of argon or nitrogen

(b) converting and protecting the hydroxyl group in **5** to methyl, tosylate or acrylate

(c) exchanging the chloride counterion in **5** to chloride, iodide, fluoride, tetrafluoroborate or hexafluorophosphate

7. A method for preparation of *n*-butyl-1-hydroalkyl Imidazolium halide of formula **6** wherein n = 0, 1, 2, 3, 4 or 5



6

R = H, CH_3, Ts, $COCH=CH_2$
X = Cl, Br, I, F, OAc, BF_4, PF_6
n = 0, 1, 2, 3, 4, 5

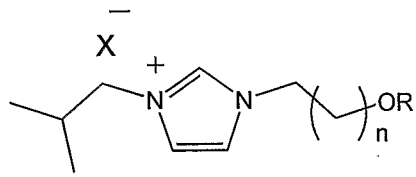
comprising the steps of:

(a) reacting 1-hydroxyalkyl imidazole **1** (n = 0, 1, 2, 3, 4, 5) with *n*-butyl chloride in refluxing tetrahydrofuran, in anhydrous condition and blanket of argon or nitrogen

(b) converting and protecting the hydroxyl group in **6** to methyl, tosylate or acrylate

(c) exchanging the chloride counterion in **6** to chloride, iodide, fluoride, tetrafluoroborate or hexafluorophosphate

8. A method for preparation of 3-*iso*-butyl-1-hydroxyalkyl imidazolium iodide of formula **7** wherein n = 0, 1, 2, 3, 4 or 5



7

R = H, CH_3, Ts, $COCH=CH_2$
X = Cl, Br, I, F, OAc, BF_4, PF_6
n = 0, 1, 2, 3, 4, 5

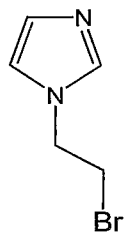
comprising the steps of:

(a) reacting 1-hydroxyalkyl imidazole **1** (n = 0, 1, 2, 3, 4, 5) with *iso*-butyl iodide in refluxing tetrahydrofuran, in anhydrous condition and blanket of argon or nitrogen

(b) converting and protecting the hydroxyl group in **7** to methyl, tosylate or acrylate

(c) exchanging the chloride counterion in **7** to chloride, bromide, fluoride, tetrafluoroborate or hexafluorophosphate

9. A method for preparation of 1-bromoethyl imidazole of formula **8**



8

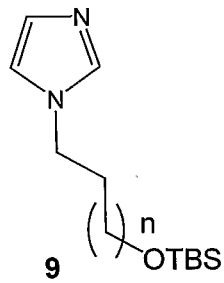
comprising the steps of:

(a) reacting 1-vinyl imidazole and 9-borabicyclo[3.3.1]nonane (9-BBN) in refluxing tetrahydrofuran followed by sodium hydroxide and 30% hydrogen peroxide treatment

(b) converting the hydroxyl group in **1** to a tosylate leaving group with tosyl chloride and anhydrous pyridine

(c) reacting the resulting product of claim 9(b) with lithium bromide in anhydrous acetone to give the respective 1-bromoethyl imidazole (**8**)

10. A method for preparation of 1-bromoalkyl imidazole of formula **9** wherein n = 0, 1, 2, 3 or 4



9

comprising the steps of:

(a) coupling the 1-bromoethyl imidazole (**8**) in Grignard reagent $TBSO(CH_2)_nMgCl$, wherein n = 0, 1, 2, 3, or 4, in the presence of coupling reagent such as nickel(II) chloride/1,3-butadiene or dilithium tetrachlorocuprate

11. The use of regenerative imidazolium reagents of claim 1 for halogenation of metals in a solid-support.

12. The use of regenerative imidazolium reagents of claim 1 for halogenation of metals in free hydroxyl form dissolved in water or polar organic solvents such as dimethyl sulfoxide, tetrahydrofuran, dioxane or alcohols.

13. The use of imidazolium reagents of claim 1 as reference electrolytes in reference electrode.

14. The use of imidazolium reagents of claim 1 as lipophilic salts in chemical sensors.

15. The use of imidazolium reagents of claim 1 as internal reference for chemical sensors.

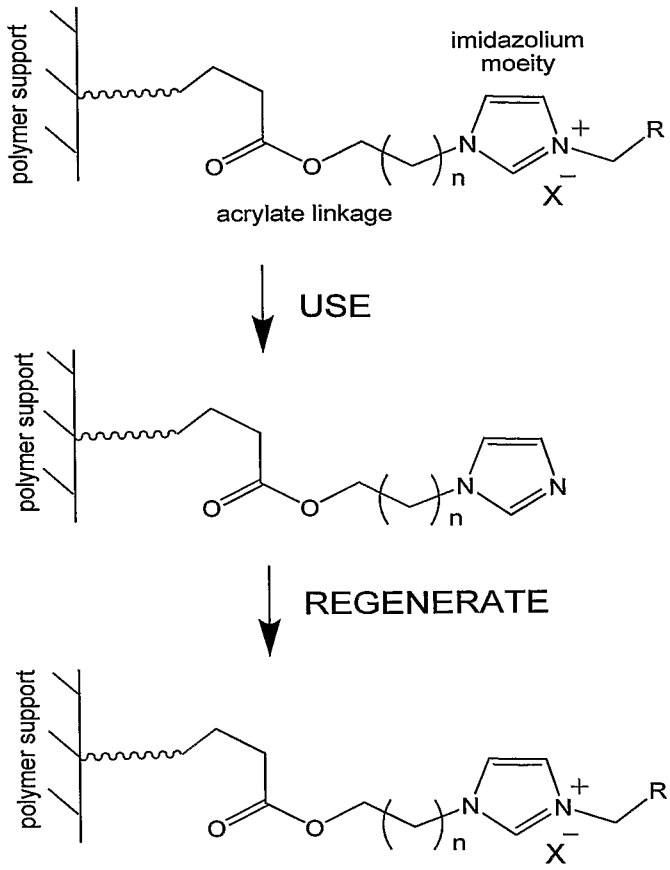

polymer support
imidazolium moeity
acrylate linkage
USE
REGENERATE

FIGURE 1

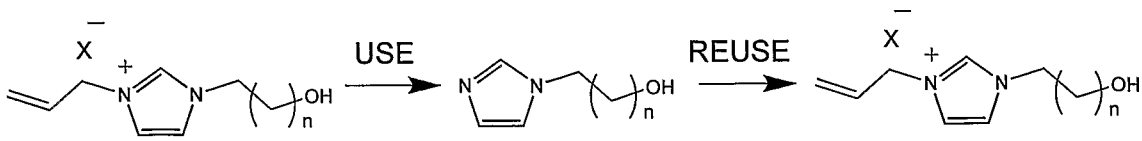


FIGURE 2