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(54) Titre : SOLVANTS A TRANSFORMATION REVERSIBLE ET METHODES D'UTILISATION
(54) Title: SWITCHABLE SOLVENTS AND METHODS OF USE THEREOF

(57) Abrégé/Abstract:
A solvent that reversibly converts from a nonionic liquid mixture to an ionic liquid upon contact with a selected trigger, e.g., contact with CO_2, is described. In preferred embodiments, the ionic solvent is readily converted back to the nonionic liquid mixture. The nonionic liquid mixture includes an amidine or guanidine or both, and water, alcohol, or a combination thereof. Some embodiments require increased pressure to convert, others convert at 1 atmosphere.

Abstract

A solvent that reversibly converts from a nonionic liquid mixture to an ionic liquid upon contact with a selected trigger, e.g., contact with CO_2, is described. In preferred embodiments, the ionic solvent is readily converted back to the nonionic liquid mixture. The nonionic liquid mixture includes an amidine or guanidine or both, and water, alcohol, or a combination thereof. Some embodiments require increased pressure to convert, others convert at 1 atmosphere.

Switchable Solvents and Methods of Use Thereof

FIELD OF THE INVENTION

The field of the invention is solvents, and specifically solvents that can be reversibly converted between ionic and nonionic forms.

BACKGROUND OF THE INVENTION

Conventional solvents have fixed physical properties which can lead to significant limitations in their use as media for reactions and separations. Many chemical production processes involve multiple reaction and separation steps, and often the type of solvent that is optimum for any one step is different from that which is optimum for the next step. Thus it is common for the solvent to be removed after each step and a new solvent added in preparation for the next step. This removal and replacement greatly adds to the economic cost and environmental impact of such processes. Therefore, there exists a need for a solvent that can change its physical properties.

Solvents are commonly used to dissolve material in manufacturing, cleaning, dyeing, extracting, and other processes. In order for a solvent to dissolve a material quickly, selectively, and in sufficient quantity, it is usually necessary for the solvent to have particular physical properties. Examples of such properties include dielectric constant, polarizability, acidity, basicity, viscosity, volatility, hydrogen-bond donating ability, hydrogen-bond accepting ability and polarity. At some point in such a process after the dissolution, separation of the material from the solvent may be desired. Such a separation can be expensive to achieve, especially if the solvent is nonvolatile as is commonly the case for polar solvents.

Moderate changes in temperature and pressure cannot be used as a method for dramatically changing solvent properties as they cause only minor changes in a conventional solvent's physical properties. Some high-pressure fluids can be continuously and reversibly changed by variations in pressure. Examples include supercritical fluids such as CHF_3 (Jessop, 1999), and CO_2-expanded liquids such as

subcritical mixtures of CO_2 and organic liquid (Subramaniam, 2002). A disadvantage of such fluids is the pressure required (greater than 25 bar and often greater than 50 bar) causes added expense, inconvenience and risk.

There is a need for liquids that are able to switch by application of a trigger from one form with a first set of physical properties to another form with a second and different set of physical properties.

SUMMARY OF THE INVENTION

In a first broad aspect, the invention provides switchable solvents and methods of preparing and using such solvents. The solvents are based on amidine or guanidine and switch between a neutral form and a charged form (amidinium or guanidinium) in response to selected trigger. When prepared as described hereinbelow, the charged form provides an ionic liquid below 100 °C, e.g., at room temperature. The trigger to change from neutral form to charged form may be exposure of the neutral form to CO_2, CS_2, or COS. Given its convenience, CO_2 is especially preferred. In preferred embodiments, solvents of the invention are not only switchable, but reversibly so, and removal of the trigger, e.g., removing CO_2, causes the charged form to switch to the neutral form.

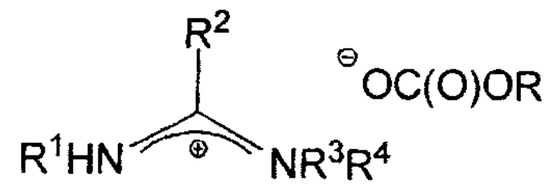
In a second broad aspect, the invention provides switchable solvents and methods of preparing and using such solvents, where the solvents are based on amidine or guanidine and switch between a first form with no local charges and a second, zwitterionic form in response to selected trigger. The trigger to change from first form to second, zwitterionic form may be exposure of the first form to CO_2, CS_2, or COS. Given its convenience, CO_2 is especially preferred. Preferably, a solvent according to this aspect of the invention is not only switchable, but reversibly so, and removal of the trigger, e.g., removing CO_2, causes the second, zwitterionic form to switch to the first form.

It should be understood that it is appropriate for purposes of the present disclosure to call removal of a first trigger a “trigger” itself, in that it causes a change in properties of the compound in question.

An aspect of the invention is a solvent that is an ionic liquid whose ionic character is changed such that it becomes a nonionic liquid in response to a trigger. Another aspect of the invention is a solvent that is a nonionic liquid whose nonionic character is changed such that it becomes an ionic liquid in response to a trigger.

According to a further aspect, the invention provides an ionic liquid that is formed by the reaction of carbon dioxide with a amidine or guanidine and water. It is reasonable to expect that these reactions are reversible; however, reversibility has not been observed to date by bubbling a said guanidinium with nitrogen or argon to remove CO_2.

In one aspect, the invention provides an ionic liquid of formula (2)



(2)

where R is alkyl, alkenyl, alkynyl, aryl, silyl, or siloxyl, and may be linear, branched, or cyclic, and may be substituted or unsubstituted; R^1, R^2, R^3, and R^4 are independently H; a substituted or unsubstituted C_1 to C_{10} alkyl group that is linear, branched, or cyclic; a substituted or unsubstituted C_nSi_m group where n and m are independently a number from 0 to 10 and n + m is a number from 1 to 10; a substituted or unsubstituted aryl group optionally containing one or more {-Si$(R^6)_2$-O-} units; or a substituted or unsubstituted heteroaryl group optionally containing one or more {-Si$(R^6)_2$-O-} units; and R^6 is a substituted or unsubstituted alkyl, aryl, heteroaryl, or alkoxy moiety. In certain embodiments, R^1, R^3, and R^4 are not hydrogen.

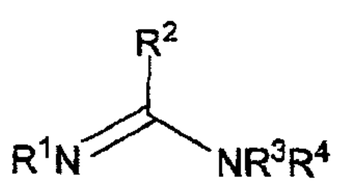
In another aspect, the invention provides an ionic liquid that is made by a method comprising the steps of: mixing a compound with alcohol, water or a combination thereof, where the compound is of the formula (1):

(1)

where R^1, R^2, R^3, and R^4 are independently H; a substituted or unsubstituted C_1 to C_{10} alkyl group that is linear, branched, or cyclic; a substituted or unsubstituted C_nSi_m group where n and m are independently a number from 0 to 10 and n + m is a number from 1 to 10; a substituted or unsubstituted aryl group optionally containing one or more $\{-Si(R^6)_2-O-\}$ units; or a substituted or unsubstituted heteroaryl group optionally containing one or more $\{-Si(R^6)_2-O-\}$ units; and R^6 is a substituted or unsubstituted alkyl, aryl, heteroaryl, or alkoxy moiety; contacting the mixture with carbon dioxide, CS_2, or COS; and obtaining the ionic liquid. In certain embodiments, R^1, R^3, and R^4 are not hydrogen.

In certain embodiments of the previous two aspects, the compound and the alcohol, water or combination thereof, are present in approximately equimolar amounts.

In another aspect, the invention provides a method of making an ionic liquid, comprising the steps of: mixing a compound with alcohol, water or a combination thereof where the compound is of the formula (1):



(1)

where R^1, R^2, R^3, and R^4 are independently H; a substituted or unsubstituted C_1 to C_{10} alkyl group that is linear, branched, or cyclic; a substituted or unsubstituted C_nSi_m group where n and m are independently a number from 0 to 10 and n + m is a number from 1 to 10; a substituted or unsubstituted aryl group optionally containing one or more $\{-Si(R^6)_2-O-\}$ units; or a substituted or unsubstituted heteroaryl group optionally containing one or more $\{-Si(R^6)_2-O-\}$ units; and R^6 is a substituted or unsubstituted alkyl, aryl, heteroaryl, or alkoxy moiety; contacting the mixture with carbon dioxide; and obtaining the ionic liquid.

The alcohol may be ROH, where R is alkyl, alkenyl, alkynyl, aryl, silyl, or siloxyl, and may be linear, branched, or cyclic, and may be substituted or unsubstituted. The alcohol may be a primary or a secondary alcohol.

In another aspect, the invention provides a method of separating a solute from an alcoholic solution comprising the steps of: adding to an alcoholic solution an amount of a compound of formula (1) that is about equimolar to the amount of alcohol in the alcoholic solution; contacting the solution with carbon dioxide to convert the solution to a first component of ionic liquid and a second component of solute; and separating the first and second components to isolate the solute.

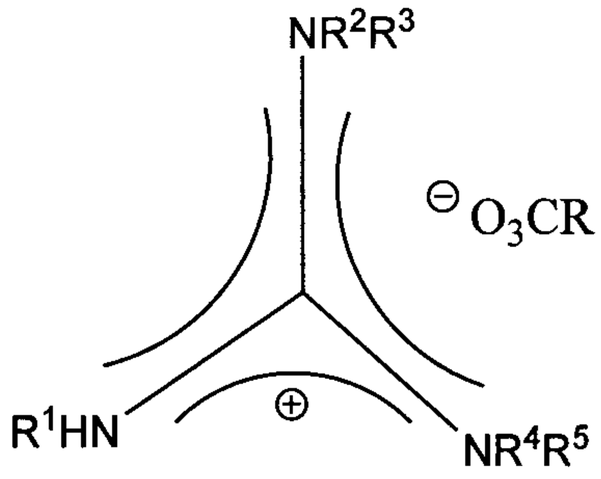
In a further aspect, the invention provides a method for separating a desired liquid from a mixture of an alcohol and the desired liquid, comprising the steps of: adding a compound of formula (1) to a mixture of an alcohol and a desired liquid; contacting the mixture with carbon dioxide to convert the alcohol and the compound to an ionic liquid; and separating the ionic liquid and the desired liquid to isolate the desired liquid, wherein the desired liquid is not reactive with the compound in the presence of the carbon dioxide.

In another aspect, the invention provides a method for separating a desired liquid from a mixture of water and the desired liquid, comprising the steps of: adding a compound of formula (1) to a mixture of water and the desired liquid; contacting the mixture with carbon dioxide to convert the water and the compound to an ionic liquid; and separating the ionic liquid and the desired liquid to isolate the desired liquid, wherein the desired liquid is not reactive with the compound in the presence of the carbon dioxide.

In another aspect, the invention provides a method for converting an ionic liquid to a nonionic liquid, comprising the steps of: providing an ionic liquid of formula (1), where R^1, R^3, and R^4 are not H, removing carbon dioxide from the ionic liquid; and obtaining the nonionic liquid. Removing carbon dioxide may comprise one or more of: heating the ionic liquid, and contacting the ionic liquid with a nonreactive gas that contains substantially no carbon dioxide.

In a further aspect, the invention provides an ionic liquid having the general formula (2), wherein the ionic liquid reversibly converts to a nonionic liquid when carbon dioxide is removed, and wherein the nonionic liquid converts to the ionic liquid upon contact with carbon dioxide. Carbon dioxide may be removed by contacting the ionic liquid with a gas that contains substantially no carbon dioxide. Carbon dioxide may be removed by contacting the ionic liquid with a gas that contains substantially no CO_2, CS_2, or COS.

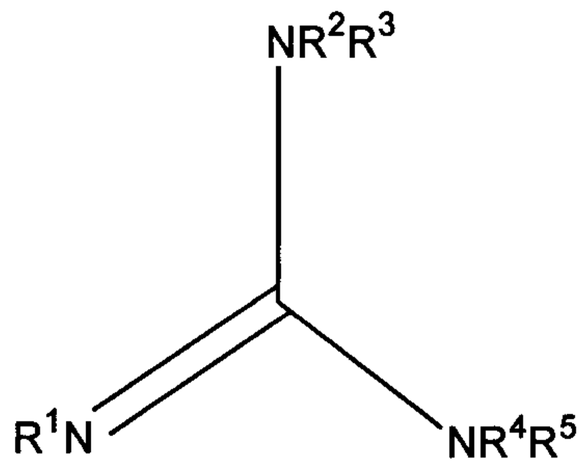
In yet a further aspect, the invention provides an ionic liquid of formula (4)



(4)

where R is alkyl, alkenyl, alkynyl, aryl, silyl, siloxyl, and may be linear, branched, cyclic, and may be substituted or unsubstituted; R^1, R^2, R^3, R^4, and R^5 are independently H; a substituted or unsubstituted C_1 to C_{10} alkyl group that is linear, branched, or cyclic; a substituted or unsubstituted C_nSi_m group where n and m are independently a number from 0 to 10 and n + m is a number from 1 to 10; a substituted or unsubstituted aryl group optionally containing one or more {-Si(R^6)$_2$-O-} units; or a substituted or unsubstituted heteroaryl group optionally containing one or more {-Si(R^6)$_2$-O-} units; and R^6 is a substituted or unsubstituted alkyl, aryl, heteroaryl, or alkoxy moiety. In certain embodiments, R, R^1, R^2, R^3, R^4, and R^5 are not hydrogen.

In a further aspect, the invention provides an ionic liquid that is made by a method comprising the steps of: mixing a compound with an alcohol, water or a combination thereof, where the compound is of the formula (3):



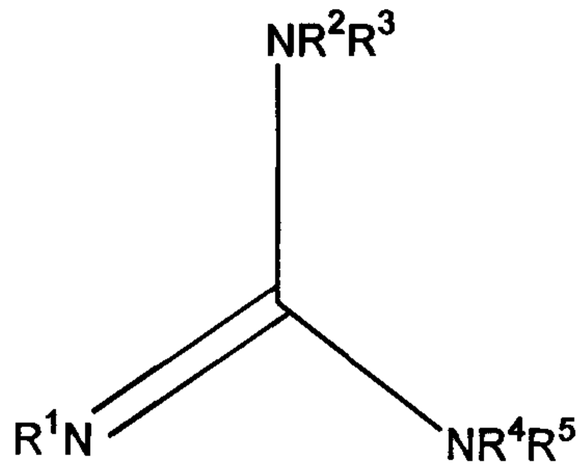
(3)

where R^1, R^2, R^3, R^4 and R^5 are independently H; a substituted or unsubstituted C_1 to C_{10} alkyl group that is linear, branched, or cyclic; a substituted or unsubstituted C_nSi_m group where n and m are independently a number from 0 to 10 and n + m is a number from 1 to 10; a substituted or unsubstituted aryl group optionally containing one or more {-Si(R^6)$_2$-O-} units; or a substituted or unsubstituted heteroaryl group optionally containing one or more {-Si(R^6)$_2$-O-} units; and R^6 is a substituted or unsubstituted alkyl,

aryl, heteroaryl, or alkoxy moiety; contacting the mixture with carbon dioxide, CS_2, or COS, and obtaining the ionic liquid. In certain embodiments, R^1, R^2, R^3, R^4, and R^5 are not hydrogen.

In certain embodiments of the previous two aspects, the compound and the alcohol, water or combination thereof, are present in approximately equimolar amounts.

In another aspect, the invention provides a method of making an ionic liquid, comprising the steps of: mixing a compound with alcohol, water or a combination thereof where the compound is of the formula (3):



(3)

where R^1, R^2, R^3, and R^4 are independently H; a substituted or unsubstituted C_1 to C_{10} alkyl group that is linear, branched, or cyclic; a substituted or unsubstituted C_nSi_m group where n and m are independently a number from 0 to 10 and n + m is a number from 1 to 10; a substituted or unsubstituted aryl group optionally containing one or more $\{-Si(R^6)_2-O-\}$ units; or a substituted or unsubstituted heteroaryl group optionally containing one or more $\{-Si(R^6)_2-O-\}$ units; and R^6 is a substituted or unsubstituted alkyl, aryl, heteroaryl, or alkoxy moiety; contacting the mixture with carbon dioxide; and obtaining the ionic liquid.

The alcohol may be ROH, where R is alkyl, alkenyl, alkynyl, aryl, silyl, or siloxyl, and may be linear, branched, or cyclic, and may be substituted or unsubstituted. The alcohol may be a primary or a secondary alcohol.

In another aspect, the invention provides a method of separating a solute from an alcoholic solution comprising the steps of: adding to the solution an amount of a compound of formula (3) that is about equimolar to the amount of alcohol in the alcoholic solution; contacting the solution with carbon dioxide to convert the solution to a first component of ionic liquid and a second component of solute; and separating the first and second components to isolate the solute.

In another aspect, the invention provides a method for separating a desired liquid from a mixture of an alcohol and the desired liquid, comprising the steps of: adding a compound of formula (3) to a mixture of an alcohol and a desired liquid; contacting the mixture with carbon dioxide to convert the alcohol and the compound to an ionic liquid; separating the ionic liquid and the desired liquid to isolate the desired liquid, wherein the desired liquid is not reactive with the compound in the presence of the carbon dioxide.

In another aspect, the invention provides a method for separating a desired liquid from a mixture of water and the desired liquid, comprising the steps of: adding a compound of formula (3) to a mixture of water and the desired liquid; contacting the mixture with carbon dioxide to convert the water and the compound to an ionic liquid; and separating the ionic liquid and the desired liquid to isolate the desired liquid, wherein the desired liquid is not reactive with the compound in the presence of the carbon dioxide.

In a further aspect, the invention provides a method for converting an ionic liquid to a nonionic liquid, comprising the steps of: providing an ionic liquid of formula (4) or an ionic liquid made from the compound of formula (3), where R, R^1, R^2, R^3, R^4, and R^5 are not H, removing carbon dioxide from the ionic liquid; and obtaining the nonionic liquid. Removing carbon dioxide may comprise one or more of: heating the ionic liquid, and contacting the ionic liquid with a nonreactive gas that contains substantially no carbon dioxide.

In a further aspect, the invention provides an ionic liquid having the general formula (4), wherein the ionic liquid reversibly converts to a nonionic liquid when carbon dioxide is removed, and wherein the nonionic liquid converts to the ionic liquid upon contact with carbon dioxide. Carbon dioxide may be removed by contacting the ionic liquid with a gas that contains substantially no carbon dioxide. Carbon dioxide may be removed by contacting the ionic liquid with a gas that contains substantially no CO_2, CS_2, or COS.

In yet a further aspect, the invention provides use of an ionic liquid of formula (2) or (4), or made from a compound of formula (1) or (3), as a sensor of CO_2, CS_2, or COS.

In a further aspect, the invention provides use of an ionic liquid of formula (2) or (4), or made from a compound of formula (1) or (3), as a detector of CO_2, CS_2, or COS.

In a further aspect, the invention provides use of an ionic liquid of formula (2) or (4), or made from a compound of formula (1) or (3), as a chemical switch.

In a further aspect, the invention provides use of an ionic liquid of formula (2) or (4), or made from a compound of formula (1) or (3), to conduct electricity.

BRIEF DESCRIPTION OF THE DRAWINGS

Embodiments of the invention will now be described, by way of example, with reference to the accompanying drawings.

Figure 1 shows a chemical reaction equation and a schematic of the reaction. The chemical reaction equation shows DBU (1,8-diazabicyclo-[5.4.0]-undec-7-ene) and an alcohol on the left hand side and amidinium alkyl carbonate on the right hand side. This reaction can be reversed, as indicated. The schematic shows the same reaction wherein the nonpolar liquid mixture of DBU and the alcohol are on the left side under a blanket of N_2. The ionic liquid amidinium alkyl carbonate product is shown on the right side under a blanket of carbon dioxide.

Figure 2 graphically presents the polarity of nonionic liquid mixtures of equimolar amounts of DBU and C3 to C10 alcohols in the lower curve (♦); and the polarity of the corresponding ionic liquids that result from reaction of the liquid mixtures with CO_2 gas at 1 bar, in the upper curve (■). The polarity is indicated by the wavelength of maximum absorbance of dissolved solvatochromic dye Nile Red.

Figure 3 graphically presents the melting temperature of ionic liquids that are formed by the reaction of CO_2 with equimolar mixtures of DBU and C1 to C10 alcohols.

Figure 4 shows a schematic of the miscibility test described in Example 2 wherein decane is miscible with alcohol and DBU on the left side and is immiscible with the corresponding ionic liquid, $[DBUH^+][RCO3^-]$, on the right side. This separation is reversible as indicated.

Figure 5A shows a chemical scheme of N,N,N',N'-tetramethyl-N"-phenylguanidine and water reacting with carbon dioxide to form the corresponding guanidinium bicarbonate, which is an ionic liquid. 5B shows a chemical scheme of N,N,N',N'-tetramethyl-N"-(2-fluorophenyl)guanidine and water reacting with carbon dioxide to form the corresponding guanidinium bicarbonate, which is also an ionic liquid. 5C shows a schematic of these reactions as described in Example 3, wherein the guanidine in each case (denoted as "amine") is miscible with wet ether on the left side, and the guanidinium bicarbonate separates from the ether into the ionic liquid on the right side.

Figure 6A shows a chemical scheme of Me-MTBD and alcohol reacting with CO_2 to form the corresponding ionic liquid. Figure 6B shows a chemical scheme of N,N,N',N'-tetramethyl-N"-butylguanidine and methanol reacting with CO_2 to form the corresponding ionic liquid.

Figure 7 shows NMR characterization data for N,N,N',N'-tetramethyl-N"-phenylguanidine and its bicarbonate salt.

DETAILED DESCRIPTION OF THE INVENTION

As used herein, "aliphatic" refers to hydrocarbon moieties that are linear, branched or cyclic, may be alkyl, alkenyl or alkynyl, and may be substituted or unsubstituted. "Aryl" means a moiety including a substituted or unsubstituted aromatic ring, including heteroaryl moieties and moieties with more than one conjugated aromatic ring; optionally it may also include one or more non-aromatic ring. Examples of aryl moieties include, phenyl, biphenyl, naphthyl, anthryl, phenanthryl, pyrenyl, pyridyl, bipyridyl, xylyl, indolyl, thienyl, and quinolinyl.

"Substituted" means having one or more substituent moieties whose presence does not interfere with the desired reaction. Examples of substituents include alkyl, alkenyl, alkynyl, aryl, aryl-halide, heteroaryl, cyclyl (non-aromatic ring), $Si(alkyl)_3$, $Si(alkoxy)_3$, halo, alkoxyl, amino, amide, hydroxyl, thioether, alkylcarbonyl, alkylcarbonyloxy, arylcarbonyloxy, alkoxycarbonyloxy, aryloxycarbonyloxy, carbonate, alkoxycarbonyl, aminocarbonyl, alkylthiocarbonyl, phosphate, phosphate ester, phosphonato, phosphinato, cyano, acylamino, imino, sulfhydryl, alkylthio, arylthio, thiocarboxylate, dithiocarboxylate, sulfate, sulfato, sulfamoyl, sulfonamide, nitro, nitrile, azido, heterocyclyl, ether, ester, silicon-containing moieties, thioester, or a combination thereof. Preferable substituents are alkyl, aryl, heteroaryl, and ether. It is noted that aryl halides are acceptable substituents. Alkyl halides are known to be quite reactive, they are acceptable so long as they do not interfere with the desired reaction.

As used herein, "heteroatom" refers to non-carbon atoms, such as, for example, O, S, and N.

"Alcohol" means a molecule of the formula ROH, where R is alkyl, alkenyl, alkynyl, aryl, silyl, or siloxyl, and may be linear, branched, cyclic, and may be substituted or unsubstituted. Substituents are as defined above and include moieties that do not interfere with the desired reaction.

The term "switched" means that the physical properties have been modified. "Switchable" means able to be converted from a first state with a first set of physical properties to a second state with a second set of physical properties. A "trigger" is a change of reaction conditions (e.g., introduction of a gas) that causes a change in the physical properties. The term "reversible" means that the reaction can proceed in either direction (backward or forward) depending on the reaction conditions.

"Short chain aliphatic" or "lower aliphatic" refers to C_1 to C_4 aliphatic. "Long chain aliphatic" or "higher aliphatic" refers to C_5 to C_{25} aliphatic. "DBU" means 1,8-diazabicyclo-[5.4.0]-undec-7-ene. As used herein, "air that has had its carbon dioxide component substantially removed" means that the air has insufficient carbon dioxide content to interfere with the removal of carbon dioxide from the solution.

As used herein, "amidine" (picture below) refers to a molecule with a structure $R^1N=C(R^2)-NR^3R^4$, where R^1 through R^4 are aliphatic or siloxyl or aryl or aliphatic/siloxyl as discussed below. The bicarbonate salt of an amidine (picture below) is termed an "amidinium bicarbonate". An amidinium salt that has the anionic counterion [$ROCO_2^-$] is termed an "amidinium alkylcarbonate" (picture below). It should be noted that amidine as used herein also includes the structure $R^1N=CH-NR^3R^4$ (i.e., R^2 is replaced by H), where R^1 and R^3, R^4 are as discussed below.

As used herein, "guanidine" (picture below) refers to a molecule with a structure $R^1N=C(NR^2R^3)(NR^4R^5)$ where R^1 through R^5 are aliphatic or siloxyl or aryl or aliphatic/siloxyl as discussed below. The bicarbonate salt of such molecule is termed the "guanidinium bicarbonate" (picture below). A guanidinium salt that has the anionic counterion [$ROCO_2^-$] is termed "guanidinium alkylcarbonate" (picture below).

"Ionic" means containing or involving or occurring in the form of positively or negatively charged ions, i.e., charged moieties. "Zwitterionic" means having two oppositely charged groups present at different locations within the same molecule. For purposes of this disclosure, "ionic liquids" are salts that are liquid below 100 °C; such liquids are typically nonvolatile, polar and viscous. For purposes of this disclosure, "zwitterionic liquids" are zwitterionic compounds that are liquid below 100 °C. "Nonionic liquids" means liquids that do not consist primarily of molecules with formal charges such as ions. Nonionic liquids are available in a wide range of polarities and may be polar or nonpolar; they are typically more volatile and less viscous than ionic liquids.

A polar molecule is a molecule in which some separation occurs of the centres of positive and negative charge. Polar solvents are typically characterized by a dipole moment. Ionic liquids are considered to be polar solvents (Aki, 2001; Reichardt, 2005), even though a dipole may not be present, because they behave in the same manner as polar liquids in terms of their ability to solubilize polar solutes, their miscibility with other polar liquids, and their effect on solvatochromic dyes. A polar solvent is generally better than a nonpolar (or less polar) solvent at dissolving polar or charged molecules.

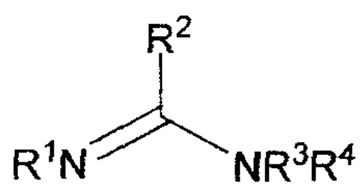
"Nonpolar" means having weak solvating power of polar or charged molecules. Nonpolar solvents are associated with either having little or no separation of charge, so that no positive or negative poles are formed, or having a small dipole moment. A nonpolar solvent is generally better than a polar solvent at dissolving nonpolar, waxy, or oily molecules.

"NMR" means Nuclear Magnetic Resonance. "Wet diethyl ether" means diethyl ether that has been purchased from a supplier and whose container has been opened to the atmosphere such that water from the air surrounding the container has entered the solvent.

The invention provides a method of separating a solute (a dissolved compound) from solution by switching the physical properties (e.g., polarity, volatility, etc.) of the solvent of the system. When the solvent has been converted into its second form, the solute may be separated from solution. Separation may include, for example, decanting, filtering, and centrifuging. The invention further provides a method for maintaining or disrupting miscibility of two liquids by using a reversible switchable solvent as one of the two liquids. When a trigger is applied, the switchable solvent's properties change and the newly-immiscible liquids separate. An embodiment of the invention provides a switchable solvent that can be reversibly and readily switched between nonionic liquid and ionic liquid forms by applying or removing CO_2.

In certain embodiments of the invention, the liquid mixture is (1) amidine and alcohol, (2) amidine and water, (3) amidine, alcohol and water, (4) guanidine and alcohol, (5) guanidine and water, (6) guanidine, alcohol and water, or (7) a nitrogen-containing organic compound that is of about equal or weaker basicity than amidine (or guanidine), and either alcohol, water or a combination thereof.

An amidine is depicted below,



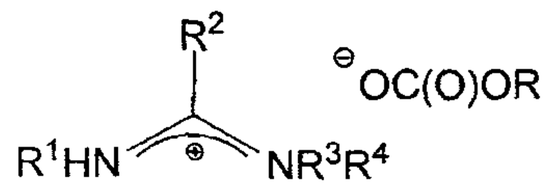
(Amidine)

where R^1, R^2, R^3, and R^4 are independently H; a substituted or unsubstituted C_1 to C_{10} alkyl group that is linear, branched, or cyclic; a substituted or unsubstituted C_nSi_m group where n and m are independently a number from 0 to 10 and n + m is a number from 1 to 10; a substituted or unsubstituted aryl group optionally containing one or more $\{-Si(R^6)_2-O-\}$ units; a substituted or unsubstituted heteroaryl group optionally containing one or more $\{-Si(R^6)_2-O-\}$ units; and

R^6 is a substituted or unsubstituted alkyl, aryl, heteroaryl, or alkoxy moiety;

wherein a substituent is independently alkyl, alkenyl, alkynyl, aryl, aryl halide, heteroaryl, non-aromatic rings, $Si(alkyl)_3$, $Si(alkoxy)_3$, halo, alkoxy, amino, ester, amide, thioether, alkylcarbonate, phosphine, thioester, or a combination thereof.

In the presence of an alcohol and carbon dioxide, such an amidine converts to an amidinium alkylcarbonate as depicted below,

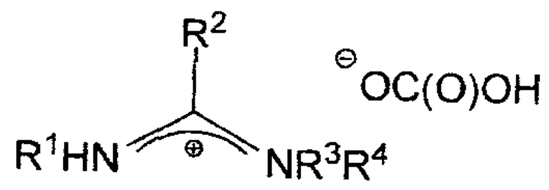


(Amidinium alkyl carbonate)

where R where R is alkyl, alkenyl, alkynyl, aryl, silyl, siloxyl, and may be linear, branched, cyclic, and may be substituted or unsubstituted;

R^1, R^2, R^3, and R^4 are as defined above .

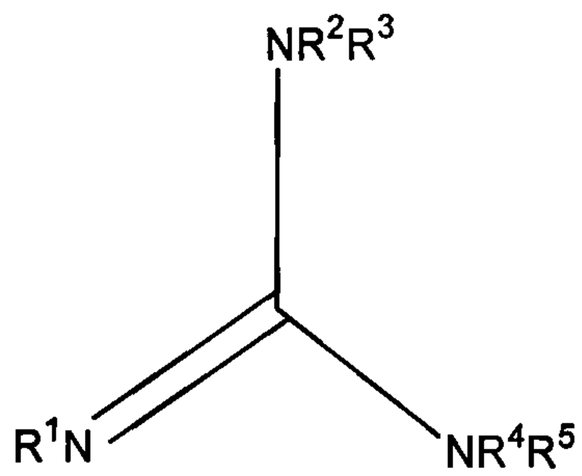
In the presence of water and carbon dioxide, such an amidine converts to an amidinium bicarbonate as depicted below,



(Amidinium bicarbonate)

where R^1, R^2, R^3, and R^4 are as defined above.

A guanidine is as shown below,



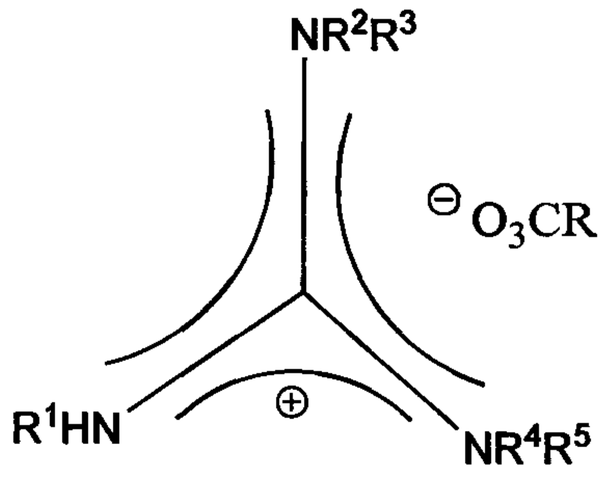
(Guanidine)

where R^1, R^2, R^3, R^4 and R^5 are independently H; a substituted or unsubstituted C_1 to C_{10} alkyl group that is linear, branched, or cyclic; a substituted or unsubstituted C_nSi_m group where n and m are independently a number from 0 to 10 and n + m is a number from 1 to 10; a substituted or unsubstituted aryl group optionally containing one or more {-Si$(R^6)_2$-O-} units; a substituted or unsubstituted heteroaryl group optionally containing one or more {-Si$(R^6)_2$-O-} units;

R^6 is a substituted or unsubstituted alkyl, aryl, heteroaryl, or alkoxy moiety;

wherein a substituent is independently alkyl, alkenyl, alkynyl, aryl, aryl halide, heteroaryl, non-aromatic rings, Si(alkyl)$_3$, Si(alkoxy)$_3$, halo, alkoxy, amino, ester, amide, thioether, alkylcarbonate, phosphine, thioester, or a combination thereof.

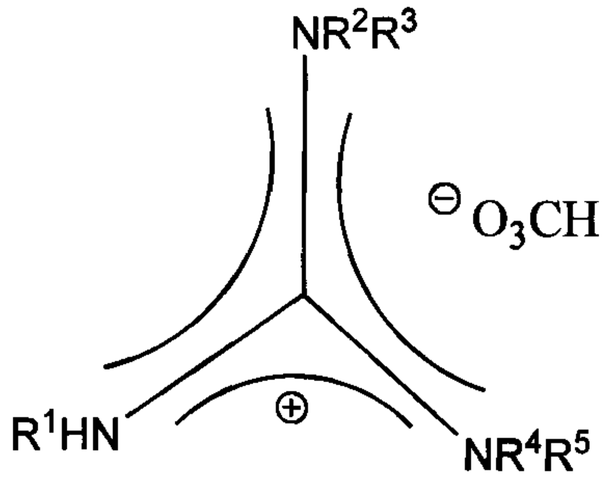
In the presence of an alcohol and carbon dioxide, such a guanidine converts to an guanidinium alkylcarbonate as depicted below,



(Guanidinium alkyl carbonate)

where R where R is alkyl, alkenyl, alkynyl, aryl, silyl, siloxyl, and may be linear, branched, cyclic, and may be substituted or unsubstituted; and R^1, R^2, R^3, R^4 and R^5 are as defined above.

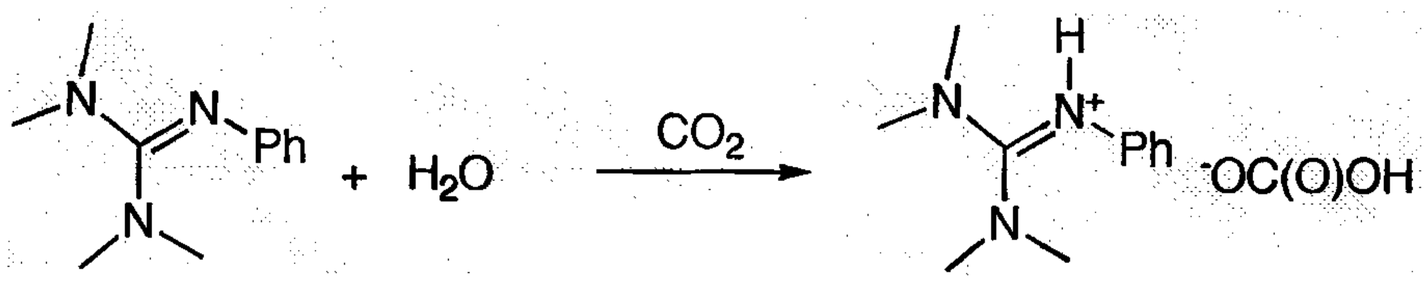
In the presence of water and carbon dioxide, such a guanidine converts to an guanidinium bicarbonate as depicted below,



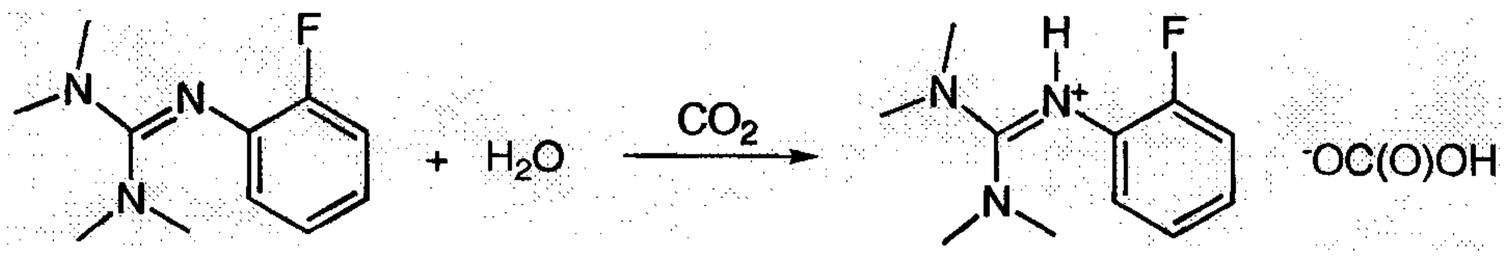
(Guanidinium bicarbonate)

where R, R^1, R^2, R^3, R^4, and R^5 are as defined above.

A switchable solvent was formed by reacting the guanidine base N,N,N',N'-tetramethyl-N"-phenylguanidine with carbon dioxide in the presence of water (see the reaction scheme below, and Example 3).



Analogously, a switchable solvent was formed by reacting the guanidine base N,N,N',N'-tetramethyl-N"-(2-fluorophenyl)guanidine with carbon dioxide in the presence of water (see the reaction scheme below, and Example 3).



Referring to Figure 1, a chemical scheme and schematic drawing are shown for a switchable solvent system of the amidine DBU and an alcohol, see Example 1.

Figure 2 graphically depicts the polarity of the nonionic liquid mixtures of DBU and C1 to C10 n-alcohols and the ionic liquids formed after exposure to carbon dioxide. The graph in Figure 2 conveys polarity by displaying the wavelength of maximum absorbance of dissolved solvatochromic dye Nile Red for each system.

Figure 3 shows the melting temperature of ionic liquids formed by reacting CO_2 with equimolar mixtures of DBU with n-alcohols of varying lengths of carbon chains, as indicated.

Figure 4 shows a schematic of the miscibility of decane with the nonionic and ionic forms of DBU and alcohol. The nonionic liquid mixture is miscible with decane. The ionic liquid is immiscible with decane. This separation is reversible as indicated. The same behaviour was observed with hexane in place of decane for a DBU/alcohol system. It was observed that the chosen alcohol must not have too long an alkyl chain, or such separation will not be observed; the alcohol's alkyl chain must be shorter than 10 carbons for the ionic form to be immiscible with hexane.

Figure 5A shows a chemical scheme of N,N,N',N'-tetramethyl-N"-phenylguanidine and water reacting with carbon dioxide to form the corresponding guanidinium bicarbonate. Figure 5B shows a chemical scheme of N,N,N',N'-tetramethyl-N"-(2-fluorophenyl)guanidine and water reacting with carbon dioxide to form the corresponding guanidinium bicarbonate. A schematic at Figure 5C depicts the experiment described in Example 3 where the guanidine and wet diethyl ether react with carbon dioxide to form a liquid ionic salt at the bottom of the vessel and diethyl ether at the top of the vessel, under a blanket of CO_2. This reaction is not reversible by the simple application of N_2 or argon.

Figure 6A shows a chemical scheme of 1,3,4,6,7,8 - hexahydro-1-methyl-2H-pyrimido [1, 2-a] pyrimidine "Me-MTBD" in alcohol reacting with CO_2 to form the corresponding salt (1,3,4,6,7,8 - hexahydro-1-methyl-2H-pyrimido [1, 2-a] pyrimidinium hexylcarbonate). This reaction is not reversible by the simple application of heat. Figure 6B shows a chemical scheme of N,N,N',N'-tetramethyl-N"-butylguanidine and methanol reacting with CO_2 to form the corresponding ionic liquid.

Figure 7 shows NMR characterization data for N,N,N',N'-tetramethyl-N"-phenylguanidine and its bicarbonate salt.

As described in the working examples, several ionic liquids have been formed according to the invention by reacting carbon dioxide with amidines or guanidines and alcohols or water. An advantage of the alcohol system is that the reverse reactions are readily effected by removing the carbon dioxide from the ionic liquid by flushing the system with a non-toxic gas that is substantially free of CO_2. The alcohol system is therefore advantageous to chemical processes wherein reversibility of the solvent switching is desirable. An advantage of the water system is the rapid rate of reaction to form the bicarbonate ionic liquids from the nonionic liquids. Due to this fast rate of reaction relative to the alcohol system, it is postulated that if a mixture of water and alcohol is used, the water will be used up prior to the consumption of the alcohol. This selectivity may have applications in industry in processes where it is desirable to remove water from solvents. If the quantity of reactant was known, this method may be useful for removing water from alcohols as well. Similarly, consumption of alcohol in a solvent mixture to form a nonionic liquid as described may be desirable.

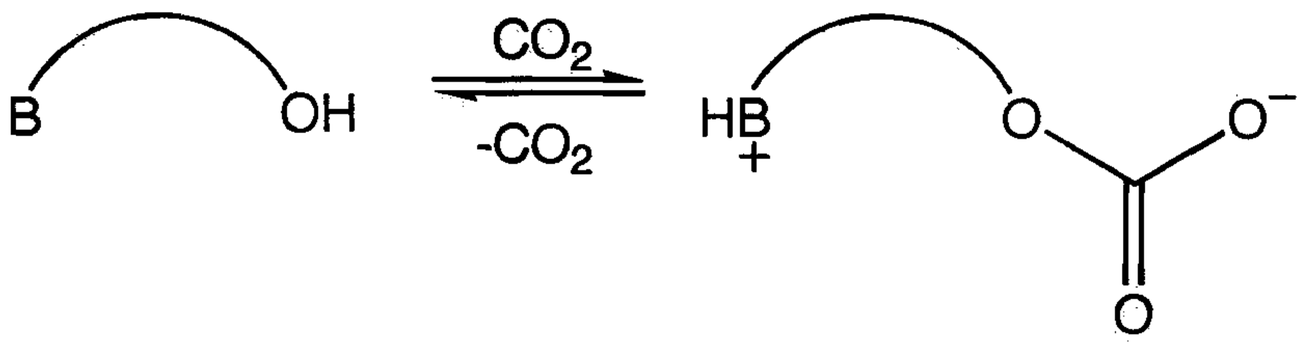
Compounds of the invention may have higher aliphatic (C_5-C_{20}) and/or siloxyl groups, however, higher aliphatic groups may cause a compound to be waxy and non-liquid at room temperature. Preferred embodiments of the invention are liquid at room temperature. Also, as the length of an aliphatic and/or siloxyl group increases, the gap between the polarity of the solvent in its two states is diminished. For these reasons, preferred aliphatic and/or siloxyl chain length is 1 to 6. A siloxyl group contains {-$Si(R^6)_2$-O-} units, where R^6 is a substituted or unsubstituted alkyl, aryl, heteroaryl, or alkoxy moiety. It should be understood that a compound of the invention may have an aliphatic/siloxyl group which is a combination of hydrocarbon and siloxyl units. A compound having a group that includes an ether or ester moiety is also encompassed by the invention. In preferred embodiments, the aliphatic/siloxyl group is alkyl. Aliphatic/siloxyl groups may be substituted with one or more moieties such as, for example, a substituent is independently alkyl, alkenyl, alkynyl, aryl, aryl halide, heteroaryl, non-aromatic rings, $Si(alkyl)_3$, $Si(alkoxy)_3$, halo, alkoxy, amino, ester, amide, thioether, alkylcarbonate, phosphine, thioester, or a combination thereof. Reactive substituents such as alkyl halide, carboxylic acid, anhydride, aldehyde and acyl chloride are not preferred.

In other embodiments of the invention all of the $R^{1\text{-}5}$ groups of the compounds of the invention are not higher aliphatic/siloxyl; they are lower aliphatic/silyl groups, and are preferably small, nonpolar and non-reactive. Examples of such groups include lower

alkyl (C_1 to C_4) groups. Preferred examples of the lower aliphatic/silyl groups are CH_3, CH_2CH_3, $CH(CH_3)_2$, $C(CH_3)_3$, $Si(CH_3)_3$, and phenyl. Monocyclic, or bicyclic ring structures, such as, for example, DBU, are also preferred.

In certain embodiments, the amidine or guanidine does not have any N-H bonds. In preferred embodiments, conversion of the liquid mixture to an ionic liquid is complete. In certain embodiments, the conversion to ionic liquid is not complete; however, a sufficient amount of the liquid mixture is converted to the ionic liquid form to change the properties of the liquid. Analogously, in some embodiments, the conversion of ionic liquid back to the nonionic liquid may not be complete; however a sufficient amount of the ionic liquid is converted to the nonionic liquid mixture to cause a useful change in the properties of the liquid.

In other embodiments, an amidine moiety (or guanidine moiety or other nitrogen-containing organic moiety) is present within the same molecule as an alcohol moiety, such that the molecule converts into a zwitterionic species in the presence of CO_2. Preferably, the zwitterionic form of the compound converts back to its uncharged form when the CO_2 is removed. A chemical scheme depicting the formation of a zwitterionic ionic liquid is depicted below, where B represents an organic base such as amidine or guanidine.



It should be understood that the invention further encompasses a combination of amidines, a combination of guanidines, and a combination of amidines and guanidines that react to form ionic liquids in the presence of water or alcohol, or a combination thereof, and in the presence of CO_2, CS_2, COS, or a combination thereof, as discussed herein. Similarly, a combination of nitrogen-containing organic compounds, with or without amidines or guanidines, are also included in the invention.

Preferably, the choice of alcohol should complement the amidine or guanidine being used in each system. Alcohols that were tested in a system of DBU and CO_2 were 1-propanol, 1-butanol, 1-hexanol, 1-octanol, 2-octanol, and 1-decanol (see Example 1).

All of these systems formed viscous ionic liquids at room temperature. Miscibility data for the ionic liquids with traditional nonpolar solvents is presented in Table 1. The ionic liquids were thoroughly characterized spectroscopically by NMR and the NMR data is presented in Tables 2 and 4. Analogous data for unreacted alcohols is presented in Tables 3 and 5 for ease of comparison. The ionic liquids prepared from 1-octanol and 1-decanol appeared liquid at room temperature upon preparation. However, subsequent melting point tests (by freezing and thawing samples) showed their melting points to be slightly above room temperature (see Figure 3). In contrast, the salts prepared by the reaction of CO_2 with an equimolar mixture of DBU and water (Perez, 2004), DBU and methanol (Main, 2001; Munshi, 2002) and DBU and ethanol formed white solids at room temperature (T_{dec} was 104 - 108 ˚C for bicarbonate). In addition, 3-ethyl-3-pentanol, a tertiary alcohol, did not react with CO_2 and DBU, either in neat form or in $CDCl_3$.

Exposure of a 1:1 mixture of the two miscible nonionic liquids, DBU and 1-hexanol, to gaseous CO_2, at 1 atmosphere, caused a conversion to an ionic liquid (see Figure 1 for the chemical scheme and Example 1 for procedural details). This exothermic reaction caused a marked increase in the viscosity of the resultant liquid. NMR data for the n-hexanol/DBU system is presented in Table 6. The detection of the hexylcarbonate anion was confirmed by mass spectroscopy as described in Example 1A.The ionic liquid was converted back into a nonionic liquid by bubbling argon through the liquid at room temperature. The same reaction was also performed at 50˚C; it occurred more rapidly at the higher temperature.

Conversion between a nonionic liquid and an ionic liquid results in a change in the properties of the solvent. As depicted in Figure 4, the nonionic liquid mixture of 1-hexanol and DBU under N_2 was miscible with decane, which is a nonpolar solvent. The ionic liquid that was formed from 1-hexanol/DBU/CO_2 was immiscible with decane. Thus CO_2 and N_2 at 1 bar can be used as triggers of immiscibility and miscibility, respectively (see Table 1). Equimolar mixtures of DBU with 1-butanol, 1-hexanol and 1-octanol exhibited the same behaviour with hexane as was described above for decane. The nonionic forms (while under N_2) were miscible. The ionic forms (while under CO_2) were immiscible. However, miscibility was restored when N_2 was bubbled through the mixtures. By contrast, a 1:1 mixture of DBU and 1-decanol was miscible with hexane even when exposed to CO_2. In this case, the relatively low polarity of the ionic form, due to the length of the decyl chain in the alcohol, caused the ionic form to be sufficiently nonpolar so as to be miscible with hexane.

The CO_2/N_2 switchable system of an equimolar mixture of DBU with ethanol exhibited different behaviour from the higher alkylcarbonates discussed above. The amidinium ethylcarbonate was immiscible with hexane, toluene and ethyl acetate, and formed a separate *liquid* phase even though it is solid when pure. It is not yet understood whether this is supercooling behaviour or a melting point depression due to the presence of the extra solvent. The polarity of supercooled liquid [DBUH][O_2COEt] is far higher than that of liquid [DBUH][$O_2COC_6H_{13}$].

The polarity of the 1-hexanol/DBU 1:1 mixture was measured with the use of two solvatochromic dyes, Reichardt's dye (a pyridinium N-phenolate betaine) (Reichardt, 2003) and Nile Red. Reichardt's dye was green when dissolved in the alcohol/DBU mixtures under N_2 and appeared yellow when dissolved in the same liquids under CO_2. This colour change is likely due at least partly to protonation of the dye or hydrogen-bonding of the dye with the acidic proton of protonated DBU or carbonic acid monohexylester; for this reason we discontinued use of Reichardt's dye for this study.

Ionic solvents were made from reacting DBU and C3 to C10 alcohols with carbon dioxide. The polarities of the resultant ionic liquids are represented by the wavelength of maximum absorbance of light of Nile Red dissolved in the ionic liquids presented in Figure 2 (upper curve). Similarly, the polarities of the equimolar DBU/alcohol mixtures under N_2 are represented by the lower line in Figure 2.

The melting point of the DBU/alcohol/CO_2 ionic liquids as a function of the alcohol's chain length are depicted graphically in Figure 3. This graph shows that for room temperature applications of the switchable solvent of the invention, a carbon chain length of 3 to 6 is preferred to avoid freezing of the ionic liquid.

The switchable solvents that use water rather than alcohol as the second component of the nonionic form differ from the switchable solvents that use alcohol because the amidines, guanidines or other N-containing organic bases are usually but not necessarily immiscible with water. Thus in most cases the nonionic form of the base/water mixture would consist of two phases, one organic and one aqueous, and would merge to a single ionic liquid phase upon exposure to CO_2. This behaviour is observed in the systems described in the N,N,N',N'-tetramethyl-N"-phenylguanidine and N,N,N',N'-tetramethyl-N"-(2-fluorophenyl)guanidine schemes of Figure 5. In contrast, most base/alcohol pairs and some base/water pairs form miscible mixtures even in their nonionic forms.

The particular choice of alcohol for use with the invention depends on the amidine or guanidine compound. In the case of DBU, methanol and ethanol are not preferred when it is desired to obtain a liquid at room temperature. In contrast, propanol or a higher alcohol are suitable for DBU.

In certain embodiments of the invention, a combination of two or more alcohols are used in place of an alcohol. In some embodiments it may be preferably to have multicomponent mixtures to decrease the melting point of the resultant ionic liquid and/or modify other properties of the ionic or nonionic forms of the switchable solvent.
In some embodiments of the invention, ionic liquids or nonionic liquid mixtures are added to conventional solvent(s) in either form.

In some embodiments, the ratio of non-gaseous reactants (amidine or guanidine or similar base and alcohol, water or alcohol/water mixture) is about equimolar. This is advantageous since when the ionic liquid is prepared from this mixture, there will remain little or no unreacted reactant(s).

In other embodiments, the ratio of non-gaseous reactants is not equimolar. As a result, when the ionic liquid is formed, it is present with a reactant.

In other embodiments, carbon dioxide may be substituted by carbon disulfide (CS_2) or carbonyl sulfide (COS). Carbonyl sulfide is not preferred because of its flammability, its negative impact on human health (irritant, damage to nervous system), and its negative impact on the environment. Carbon disulfide is not preferred because of its flammability, its toxicity, and its negative impact on the environment. Nevertheless, CS_2 and COS are expected to be capable of triggering the same change in the switchable solvents as can CO_2.

Carbon dioxide may be provided from any convenient source, for example, a vessel of compressed CO_2(g) or as a product of a non-interfering chemical reaction. The ionic liquid can be converted to a nonionic liquid by removing the carbon dioxide, for example, by exposing the mixture to a non-toxic gas that contains substantially no carbon dioxide. Preferred gases that are substantially free of CO_2 include, for example, argon, N_2, argon, air that has insufficient carbon dioxide to switch the nonionic liquid mixture to ionic liquid, air with the carbon dioxide component removed. In some cases, normal air, without any removal of the existing CO_2 content, will suffice. Conveniently, such exposure is achieved by bubbling the gas through the mixture or by any other means of providing efficient contact between the liquid and gas phases. However, it is important to recognize that heating the mixture is an alternative method of driving off the

CO_2, and this method of converting the ionic liquid to nonionic liquid is also encompassed by the invention. In certain situations, especially if speed is desired, both bubbling (or other means of providing efficient contact) and heat can be employed.

Some embodiments of the invention require a pressure of CO_2 greater than 1 bar to switch the solvent from nonionic to ionic . Preferred embodiments are able to react with CO_2 at 1 bar or less to trigger the switch. High pressure switchable solvent molecules require a pressure of CO_2 greater than 1 atm to switch to ionic form and are substantially completely switched to the nonionic form by a decrease in CO_2 pressure to about 1 atm. High pressure switchable solvents may be more time efficient than atmospheric-pressure systems. These high pressure switchable solvents may differ from the atmospheric-pressure switchable solvents by a change in the steric or electronic properties of the amine base (e.g., guanidine or amidine). Such molecules may include, for example, tertiary amines, trialkylamines such as N-methylpyrrolidine, and amidines and guanidines with decreased basicity when compared to DBU such as amidines and guanidines having aryl groups directly attached to one or more of the N atoms. Alternatively, high pressure switchable solvents may differ from the atmospheric pressure switchable solvents by a change in the steric or electronic properties of the alcohol. It should be understood that the invention encompasses amidine or guanidine compounds that have lower or about equal basicities than DBU and that react with CO_2 in the presence of alcohol, water or a combination thereof under high pressure (i.e., are high pressure switchable solvent compounds).

Although the requirement for high pressure in generation of an ionic liquid can be viewed as a disadvantage, the ability to switch the properties of such a molecule rapidly by reduction of the CO_2 pressure may conversely be viewed as an advantage. For these reasons, the high pressure switchable solvent molecules may be particularly suited to some industrial processes, for example, where elevated pressures are already used or where rapid solvent switching is required.

Atmospheric pressure switchable solvents include amidines, guanidines and primary and secondary amines, each with aliphatic/siloxyl portion(s) as discussed below. If the switch to the ionic form is to be easily reversible, the amidines or guanidines are preferably peralkylated. The term "peralkylated" as used herein means that the amidine or guanidine has alkyl or other groups connected to the N atoms so that the molecule contains no N-H bonds. This lack of N-H groups is intended to avoid potentially

irreversible reactions with carbon dioxide. If the switch to the ionic form is not to be reversible, then there is no preference that the amidine or guanidine be "peralkylated".

An alternative method of preparing a high-pressure switchable solvent would be to use an alcohol that shows diminished conversion to the alkyl carbonate (in the presence of an amidine or guanidine and carbon dioxide) at 1 atm of CO_2 pressure. An example of such an alcohol is a secondary or tertiary alcohol.

An advantage of switchable solvents is that they facilitate organic syntheses and separations by eliminating the need to remove and replace solvents after each reaction step. With triggers that are capable of causing a drastic change in the solvent properties while it is still in the reaction vessel, it may be possible to use the same solvent for several consecutive reaction or separation steps. This would eliminate the need to remove and replace the solvent.

Reuse and recycling of solvents of the invention are convenient, with attendant economic benefits. The time required to switch between the ionic and nonionic forms according to the invention is short. In certain applications, it may be advantageous to convert from nonionic to ionic and then back again (or vice-versa). For example, the solvent could be made nonionic to be miscible with a nonpolar liquid, and then the solvent could be switched to its ionic form to allow for separation of the resulting two liquid components. The liquid components may or may not appear as distinct layers. Separation of the components may include decanting, or centrifuging. After separation, it may be desirable to convert the ionic form back to its nonionic form. Thus the solvent can be reused. In some embodiments it may be desirable to use the solvent in its ionic form. This molten salt form would separate from aqueous solutions when converted to its nonionic form, allowing for easy recovery and reuse of the solvent.

The invention provides a convenient system to controlling the properties of a solvent. Thus, it is useful in many industrial applications. For example, a chemical reaction that requires a polar solvent could be performed in the switchable solvent while in its ionic form. Once the reaction is complete, the solvent could be switched to its nonionic form which is substantially incapable of dissolving the product of the reaction. This would force the product to precipitate, if solid, or become immiscible, if liquid. The solvent could then be separated from the product by physical means such as, for example, filtration or decantation. If appropriate, the solvent could then be switched back to its ionic form and reused. This method allows the use of a polar solvent without the

requirement for an energy-intensive distillation step to remove the solvent. Such distillation steps are costly since many polar solvents have high boiling temperatures.

A switchable solvent would be advantageous in a two-step chemical synthesis in which the first step requires a polar solvent and the second step requires a nonpolar solvent (or vice versa). The first chemical reaction, which requires a polar solvent, could be performed in the solvent while in its ionic form, producing a chemical intermediate. Once the first reaction is complete, the solvent could be switched to its nonionic form, which is capable of maintaining the chemical intermediate in solution. The intermediate would then be converted to a desired product by a second reaction, which requires a nonpolar solvent. Traditionally, this two-step synthesis would be performed using two solvents, a polar solvent for the first step, and a nonpolar solvent for the second step. The removal of the polar solvent after the end of the first step would involve extra cost, time and energy. Thus switchable solvents as described herein can lessen the environmental impact of industrial processes, by saving time and energy normally expended during solvent substitutions, or during solvent removal from product or solute.

Switchable solvents of the invention can be useful in water/solvent or alcohol/solvent separations in biphasic chemical reactions. As seen in Figure 4, separation of a nonionic liquid from a switchable solvent may be effected by switching the switchable solvent to its ionic form. This ability to separate solvents may be useful in many industrial processes where upon completion of a reaction, one of the solvents is switched to its ionic form allowing for facile separation of the two distinct phases. Thus a switchable solvent, may be used in its nonionic state as a medium for a chemical reaction. Upon completion of the reaction, the chemical product is readily separated from solution by switching the solvent to its ionic form. The solvent can then be recovered and reused, if appropriate.

A further aspect of the invention is a nonionic liquid mixture that is largely nonconductive (or only weakly conductive) of electricity, that becomes more conductive when it is converted to its ionic form, and that this change may be reverseable. In the hexanol/DBU system described in Example 1A, conductivity of the ionic form was 20 times that of the nonionic form. Such a conductivity difference would enable the liquid to serve as an electrical switch, as a switchable medium, as a detector of CO_2 or CS_2 or COS, or as a sensor of the presence of CO_2 or CS_2 or COS. This ability of the ionic

liquid to conduct electricity may have applications in electrochemistry, in liquid switches and in sensors and/or detectors.

WORKING EXAMPLES

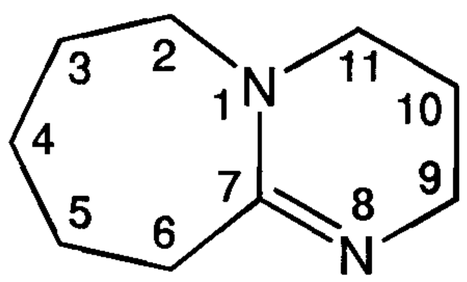
DBU (Aldrich, Oakville, Ontario, Canada, 98% grade) was refluxed over CaH_2 and distilled under reduced pressure onto 4Å molecular sieves and then deoxygenated by repeated freeze/vacuum/thaw cycles. Alcohols (99+%, anhydrous) were used as received from Aldrich. Decane (Aldrich, 99+% grade) was degassed with nitrogen prior to use. Hexanes (Fisher Scientific, HPLC grade) and Toluene (Fisher Scientific, HPLC grade) were degassed and dried by passing them through an activated alumina column under nitrogen prior to use. Ethyl acetate (Fisher Scientific, HPLC grade) was degassed with nitrogen prior to use. Supercritical grade CO_2 (99.999%, H_2O < 0.5 ppm), nitrogen (99.998%, H_2O < 3 ppm) and argon (99.998%, H_2O < 5 ppm) were used as received from Praxair Canada Inc., (Mississauga, Ontario, Canada).

Example 1. Reversible Solvent Switching in an Amidine and Alcohol System

Example 1A. Reversible Solvent Switching in a DBU and 1-Hexanol System

Dried DBU (0.60 mL, 4.0 mmol, see Figure 1) and 1-hexanol (0.50 mL, 4.0 mmol) were placed in a dry glass NMR (Nuclear Magnetic Resonance) tube in a glove box (Vacuum Atmospheres Company, Hawthorne, California) under N_2. Carbon dioxide was bubbled through the liquid via a hollow narrow-gauge stainless steel tube which was inserted in the solution within the NMR tube. The rate of bubbling was 2 bubbles per second for 1 hour. The liquid became increasingly viscous. The conductivity of the solution, measured using an immersible conductivity probe (Jenway, model 4071, available at Canadawide Scientific, Ottawa, Canada), increased more than 20 fold. The ^1H NMR spectrum of the resultant solution, although broadened due to the solution's viscosity, clearly indicated complete conversion to $[DBUH][O_2CO(CH_2)_5CH_3]$ (where "DBUH" is protonated DBU) with no residual signals for free 1-hexanol or unprotonated DBU. The ^1H NMR resonance in $CDCl_3$ attributed to the oxygen-bound methylene of the hexyl group had shifted to 3.90 ppm from 3.58 ppm (the resonance for the same methylene group in unreacted hexanol). This resonance is comparable to the corresponding chemical shifts seen for $CH_3C(O)O(CH_2)_5CH_3$ (in $CDCl_3$) at 4.05 ppm (Reynders, 1990) and dihexyl carbonate at 4.13 ppm (in CCl_4) (Sakai, 1971).

Please see the picture below for the numbering scheme for positions in the DBU structure.



Spectroscopic data for [DBUH][$O_2CO(CH_2)_5CH_3$]:

^{1}H NMR (δ, ppm, in $CDCl_3$) 3.90 (t, 2H, hexyl C1), 3.49 (m, 4H, DBUH C2 and C11), 3.43 (t, 2H, DBUH C9), 2.81 (br, 2H, DBUH C6), 2.00 (quintet, 2H, DBUH C10), 1.75 (br, 6H, DBUH C3, C4, and C5), 1.58 (quintet, 2H, hexyl C2), 1.37 (m, 2H, hexyl C3), 1.29 (br, 4H, hexyl C4 and C5), 0.87 (t, 3H, hexyl C6).

^{13}C{^{1}H} NMR (δ, ppm, in $CDCl_3$, referenced to $CDCl_3$ at 77.2 ppm) 164.9 (DBUH C7), 158.7 (O_2*C*OR), 64.6 (hexyl C1), 53.5 (DBUH C2), 48.1 (DBUH C11), 38.6 (DBUH C9), 32.3 (DBUH C6), 31.5 (hexyl C4), 29.4 (hexyl C2), 28.8 (DBUH C4), 26.8 (DBUH C3), 25.5 (hexyl C3), 24.0 (DBUH C5), 22.2 (hexyl C5), 19.7 (DBUH C10), 13.7 (hexyl C6); IR (neat) 2938 (m), 1648 (s), 1613 (s), 832 (m), 688 cm^{-1} (m).

Mass Spectroscopy of a Mass Spectroscopy Sample in Electrospray Ionization negative mode ("MS/MS (ESI, negative mode)" 145.1 (M), 101.1 (M-CO_2), 99.1 (M-H_2CO_2), 83.0 (M-H_2CO_3), 60.0 (CO_3^-), where "M" is the anion $C_6H_{13}OCO_2^-$.

For comparison, literature shows that [NBu_4][O_2COEt] has a ^{13}C{^{1}H} NMR signal for the carbonyl at 157.9 ppm in $CDCl_3$ and IR peaks at 2940, 2880 and 1670 cm^{-1} in KBr (Verdecchia, 2002).

Spectroscopic changes upon exposure of the hexanol/DBU mixture to CO_2 are presented in Tables 2, 4 and 6. Solvatochromic data measuring the polarity of the liquid before and after exposure to CO_2 are presented in Figure 2.

Reversability of the reaction was confirmed when a sample of the ionic liquid in an NMR tube was heated to 50 ˚C and argon was bubbled through the sample for 1 h. The viscosity dropped greatly. The ^{1}H NMR spectrum after this procedure was consistent with the spectra of 1-hexanol and DBU, showing no peaks for residual ionic liquid.

Exposure of [DBUH][$O_2COC_6H_{13}$] ionic liquid to moist air resulted in the appearance of a white solid within a few minutes. The white solid, washed with acetonitrile, was identified as the bicarbonate salt [DBUH][O_2COH] by IR and ^{1}H NMR (in $CDCl_3$).

Example 1B. Reversible Solvent Switching in a System of DBU and Various Alcohols.

Analogous tests as the one described in Example 1A were performed for DBU and n-chain alcohols having 1, 2, 3, 4, 6, 8 and 10 carbon atoms. The products of the DBU with the C3-C10 alcohols were liquids at room temperature as indicated in Figure 3. Preliminary tests of DBU with secondary and tertiary alcohols were not successful in obtaining complete conversion to ionic liquids. An example of a tertiary alcohol, 3-ethyl-3-pentanol, with an equimolar amount of DBU did not react with carbon dioxide. Secondary alcohols (2-octanol, (1R, 2S, 5R)-(-)-menthol and (1S)-endo – (-) borneol) reacted to form an ionic liquid, but complete conversion was not obtained. The greatest conversion of these secondary alcohols (about 64%) was obtained with 2-octanol.

In the cases of the primary n-alcohols, the ionic liquids were characterized by ^{1}H and ^{13}C NMR. The reversibility of the reaction in each case to reform DBU and the appropriate alcohol was also confirmed by ^{1}H NMR. Spectroscopic changes upon exposure of the alcohol/DBU mixtures to CO_2 are presented in Tables 2, and 4 while the unreacted alcohols' spectroscopic data is presented in Tables 3 and 5, for comparison purposes. Solvatochromic data measuring the polarity of the liquid before and after exposure to CO_2 are presented in Figure 2.

The relative polarities of the DBU/alcohol mixtures and the corresponding ionic liquids are presented graphically in Figure 2, where the y axis is the wavelength of the peak of Nile Red dye in the solvent. High polarity is represented by a greater wavelength value, and lower polarity is represented by a lower wavelength value.

The melting point of the ionic form of the switchable solvent made from DBU and an alcohol having 1 to 10 carbon atoms is presented graphically in Figure 3 wherein the y axis is the melting point and the x axis is the length of carbon chain of the R component of the salt which is derived from the alcohol.

Example 2. Miscibility Switching in a DBU and Alcohol System.

In an inert atmosphere, 26.8 mmol each of DBU (95 ppm H_2O) and 1-hexanol (26 ppm H_2O) were charged into a flame-dried flask. N-Decane (2 mL, undried) was added and was found to be miscible at room temperature; only one homogeneous liquid phase was observed. CO_2 (H_2O < 5 ppm) was slowly bubbled through the decane/1-hexanol/DBU mixture at 1 bar overnight. The resultant mixture appeared split into two separate

liquids. Argon was then bubbled through the two-phase liquid mixture for 1 h at 35 °C. After 1 h, the two liquids had merged into one liquid. A schematic representation of this reversible reaction appears in Figure 4. Similar experiments were performed with hexane in place of decane and with several alcohols (1-propanol, 1-butanol, 1-hexanol, 1-octanol, and 1-decanol) in place of 1-hexanol; similar results were obtained except that with 1-decanol, no phase split was observed even after the treatment with CO_2. Miscibility data for alcohol/DBU systems is presented in Table 1.

Example 3. Solvent Switching in a Guanidine and Water System.

An ionic liquid was formed by bubbling carbon dioxide through a solution of N,N,N',N'-tetramethyl-N"-phenylguanidine (500 mg) (see Figure 5A) in wet diethyl ether (5 mL). The liquid bicarbonate salt formed a separate liquid phase from the diethyl ether (see Figure 5C). The ionic liquid was characterized by ^{1}H NMR spectroscopy wherein the proton resonances of the guanidinium bicarbonate had shifted relative to the corresponding resonances of the unreacted N,N,N',N'-tetramethyl-N"-phenylguanidine (see Figure 7).

Similarly, an ionic liquid was formed by bubbling carbon dioxide through a solution of N,N,N',N'-tetramethyl-N"-(2-fluorophenyl)guanidine (500 mg) (see Figure 5B) dissolved in wet diethyl ether(5 mL). The liquid bicarbonate salt formed a separate liquid phase that was distinct from the diethyl ether as depicted in Figure 5. The ionic liquid was characterized by ^{1}H NMR spectroscopy wherein the proton resonances of the guanidinium bicarbonate had shifted relative to the corresponding resonances of the unreacted N,N,N',N'-tetramethyl-N"-(2-fluorophenyl)guanidine.

An ionic liquid was formed, in the absence of ether, by bubbling carbon dioxide through an equimolar mixture of water and N,N,N',N'-tetramethyl-N"-phenylguanidine. Prior to bubbling, the liquids appear as a biphasic mixture with the guanidine on the top and the water on the bottom. After bubbling, the liquid appeared as a single phase ionic liquid.

Attempts to reverse the switch to reform the nonionic guanidines of Example 3 by bubbling the ionic liquids with argon have been unsuccessful to date.

Example 4. Reversible Solvent Switching in a Guanidine and Alcohol System.

An ionic liquid was reversibly formed by bubbling carbon dioxide through a mixture of 1,3,4,6,7,8-hexahydro-1-methyl-2H-pyrimido[1,2-a]pyrimidine ("Me-MTBD", see Figure

6A), which was used as purchased from Aldrich, and 1-octanol. The formation of the ionic liquid was confirmed by ^{1}H NMR spectroscopy. The same reaction with methanol in place of octanol gave a solid product. Attempts to reverse the switch to reform Me-MTBD and 1-octanol by heating the ionic liquids have been unsuccessful to date.

An ionic liquid was reversibly formed (as described in Example 1A) by bubbling carbon dioxide through a solution of N,N,N',N'-tetramethyl-N"-butylguanidine (see Example 5 and Figure 6B) and methanol. The formation of the ionic liquid was confirmed by ^{1}H and ^{13}C NMR spectroscopy, including the ^{13}C NMR technique known as "attached proton test" (APT or DEPT). The reversibility of the reaction to reform the nonionic guanidine and methanol was confirmed by ^{1}H and ^{13}C NMR. The reversal was achieved by bubbling N_2 through the neat ionic liquid at 50 °C. The reversal was also achieved by dissolving the ionic liquid in a solvent and then bubbling N_2 through that solution. The reversal by the latter method, at room temperature, took 12 hours of bubbling in DMSO and greater than 24 hours in $CDCl_3$.

Example 5. Synthesis of N,N,N',N'-tetramethyl-N"-butylguanidine

N,N,N',N'-tetramethyl-N"-butylguanidine was prepared as follows: 9.3 g tetramethyl urea was added to 80 mL dry dichloroethane in a two-neck 250mL round-bottom-flask. 11.3 mL oxalyl chloride was added and the solution was heated at 70°C for two hours. The solvent was evaporated *in vacuo* after the solution cooled to room temperature. Residual solid was then dissolved in dry acetonitrile and cooled to 0°C. 15 mL butyl amine (1.02 eq) was slowly added. The solution was slowly warmed and allowed to reflux for one hour. Finally, the mixture was cooled to room temperature and the solvent was removed *in vacuo* to yield 9 g of a clear oil. ^{1}H ($CDCl_3$): δ (ppm): 2.99 (t, 2H); 2.62 (s, 3H); 2.53 (s, 3H); 1.39 (quintet, 2H); 1.24 (quintet, 2H); 0.78 (t, 3H). The synthesis was performed several times and the yield ranged from 37%- 70%.

Information regarding switchable solvents appears in Jessop, P. G.; Heldebrant, D. J.; Li, X.; Eckert, C.A.; Liotta, C. L. " A Reversible Ionic/Non-Ionic Switchable Solvent," *Nature* **436, 1102** (2005).

The scope of the claims should not be limited by the preferred embodiments set forth in the examples, but should be given the broadest interpretation consistent with the description as a whole.

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Table 1. Miscibility of the [DBUH][O_2COR] ionic liquids with hexane, toluene and ethyl acetate (traditional nonpolar solvents).

R of [O_2COR]	Miscible with Hexanes?	Miscible with Toluene?	Miscible with Ethyl acetate?
Ethyl	No	No	No
1-Butyl	No	Yes	Yes
1-Hexyl	No	Yes	Yes
1-Octyl	No	Yes	Yes
1-Decyl	Yes	Yes	Yes

Table 2. $^{13}C\{^{1}H\}$ NMR chemical shifts of [DBUH][O_2COR] salts in $CDCl_3$.

Carbon	**R of [$^-O_2$COR]**						
	H	ethyl	1-propyl	1-butyl	1-hexyl	1-octyl	1-decyl
[O_2<u>C</u>OR]	161.1	158.6	158.6	157.8	158.7	157.5	158.3
DBU C_2	53.2	53.5	53.9	52.9	53.5	52.6	53.3
DBU C_3	29.7	27.1	26.9	28.1	26.8	26.7	26.4
DBU C_4	28.3	28.9	28.9	23.5	28.8	23.3	23.7
DBU C_5	25.7	24.4	25.9	26.2	24.0	28.0	28.6
DBU C_6	36.6	33.1	31.5	31.0	32.3	31.8	31.7
DBU C_7	162.6	164.4	164.9	164.2	164.9	163.6	164.8
DBU C_9	43.1	39.4	38.4	38.1	38.6	38.2	38.0
DBU C_{10}	22.0	20.1	19.5	19.1	19.7	19.0	19.2
DBU C_{11}	48.5	48.2	48.5	47.5	48.1	47.2	47.8
ROH C_1	N/A	60.0	65.7	63.5	64.6	63.5	64.2
ROH C_2	N/A	15.1	31.5	31.7	29.4	28.6	28.6
ROH C_3	N/A	N/A	19.1	18.3	25.5	25.0	25.3
ROH C_4	N/A	N/A	N/A	13.0	31.5	28.0	29.0
ROH C_5	N/A	N/A	N/A	N/A	22.2	28.0	29.0
ROH C_6	N/A	N/A	N/A	N/A	13.7	30.5	29.0
ROH C_7	N/A	N/A	N/A	N/A	N/A	21.3	29.0
ROH C_8	N/A	N/A	N/A	N/A	N/A	12.8	31.1
ROH C_9	N/A	N/A	N/A	N/A	N/A	N/A	21.9
ROH C_{10}	N/A	N/A	N/A	N/A	N/A	N/A	13.4

Table 3. $^{13}C\{^{1}H\}$ NMR chemical shifts of pure n-alcohols in $CDCl_3$.

Carbon	Ethanol	Propanol	Butanol	Hexanol	Octanol	Decanol
ROH C1	58.0	64.5	62.4	62.7	62.9	62.9
ROH C2	18.3	26.0	34.8	32.7	32.9	32.8
ROH C3	na	10.2	19.0	25.4	25.8	25.9
ROH C4	na	na	13.9	31.6	29.3	29.6
ROH C5	na	na	na	22.5	29.4	29.6
ROH C6	na	na	na	14.0	31.8	29.6
ROH C7	na	na	na	na	22.7	29.4
ROH C8	na	na	na	na	14.1	32.0
ROH C9	na	na	na	na	na	22.8
ROH C10	na	na	na	na	na	14.2

Table 4. ^{1}H NMR chemical shifts of [DBUH][O_2COR] salts in $CDCl_3$.

	R of [$^{-}O_2COR$]					
Proton position	H	Ethyl	1-butyl	1-hexyl	1-octyl	1-decyl
DBU C2	3.39	3.61	3.54	3.49	3.53	3.53
DBU C3	1.72	1.74	1.73	1.75	1.70	1.76
DBU C4	1.65	1.74	1.73	1.75	1.60	1.76
DBU C5	1.72	1.74	1.73	1.75	1.75	1.76
DBU C6	2.71	2.86	2.79	2.81	2.77	2.84
DBU C9	3.39	3.42	3.40	3.43	3.39	3.43
DBU C10	1.94	2.05	2.01	2.00	2.00	2.02
DBU C11	3.39	3.61	3.54	3.49	3.53	3.53
ROH C1	na	3.91	3.88	3.90	3.88	3.89
ROH C2	na	1.19	1.6	1.58	1.58	1.59
ROH C3	na	na	1.41	1.37	1.36	1.27
ROH C4	na	na	0.92	1.29	1.28	1.27
ROH C5	na	na	na	1.29	1.28	1.27
ROH C6	na	na	na	0.87	1.28	1.27
ROH C7	na	na	na	na	1.28	1.27

ROH C8	na	na	na	na	0.88	1.27
ROH C9	na	na	na	na	na	1.27
ROH C10	na	na	na	na	na	0.88

na = not applicable.

Strongly overlapped peaks have been given identical chemical shifts.

Table 5. ^{1}H NMR chemical shifts of pure n-alcohols in $CDCl_3$.

Proton Position	EtOH	PrOH	BuOH	Hexanol	Octanol	Decanol
ROH C1	3.68	3.58	3.62	3.63	3.62	3.61
ROH C2	1.22	1.58	1.55	1.58	1.56	1.56
ROH C3	na	0.93	1.38	1.30	1.30	1.27
ROH C4	na	na	0.93	1.30	1.30	1.27
ROH C5	na	na	na	1.30	1.30	1.27
ROH C6	na	na	na	0.91	1.30	1.27
ROH C7	na	na	na	Na	1.30	1.27
ROH C8	na	na	na	Na	0.88	1.27
ROH C9	na	na	na	Na	na	1.31
ROH C10	na	na	na	Na	na	0.88

Table 6 ^{1}H NMR chemical shifts for key protons observed in n-hexanol, DBU, or mixtures of n-hexanol and DBU.

	Pure hexanol or DBU in $CDCl_3$	Nonionic Liquid		Ionic Liquid	
Solvent	$CDCl_3$	$CDCl_3$	Neat	$CDCl_3$	neat
Sample	pure	1:1 mix[a]	1:1 mix[a]	1:1 mix[a]	1:1 mix[a]
CO_2	absent	absent	absent	present	present
Protons on C1 of hexanol[b]	3.58	3.56	3.38	3.90	3.69
Protons on CH_3 of hexanol[b]	0.82	0.80	0.85	0.87	0.85
Protons on C2, C9 and C11 of DBU[b]	3.1-3.3	3.1-3.3	3.1-3.2	3.4-3.5	3.2-3.5
Protons on C6 of DBU[b]	2.38	2.37	2.28	2.81	2.75

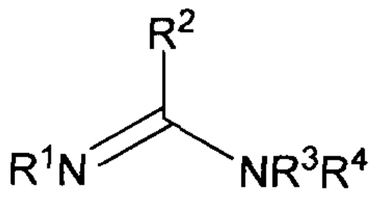
[a]1:1 mole ratio of DBU and 1-hexanol.

[b]The internal methylene protons in hexanol (1.2 to 1.5 ppm) and methylenes on C3, C4, C5, and C10 of DBU at 1.5 to 1.8 ppm are heavily overlapped with other peaks in the spectra of the mixtures.

We claim:

1. A method for separating a nonpolar liquid from a mixture, comprising:

providing a mixture comprising a nonpolar liquid, an alcohol, a compound of formula (1), and CO_2, where the compound of formula (1) is:



(1)

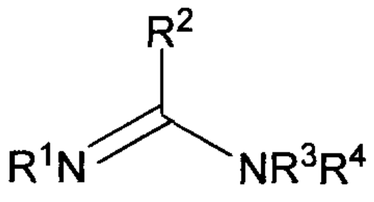
where R^1, R^2, R^3, and R^4 are independently H; a substituted or unsubstituted C_1 to C_{10} alkyl group that is linear, branched, or cyclic; a substituted or unsubstituted C_nSi_m group where n and m are independently a number from 0 to 10 and n+m is a number from 1 to 10; a substituted or unsubstituted aryl group optionally containing one or more {-Si(R^6)$_2$-O-} units; or a substituted or unsubstituted heteroaryl group optionally containing one or more {-Si(R^6)$_2$-O-} units; R^6 is a substituted or unsubstituted alkyl, aryl, heteroaryl, or alkoxy moiety; and wherein the compound of formula (1) may be a monocyclic or bicyclic ring structure;

converting the alcohol, the compound of formula (1), and the CO_2 into an ionic liquid, wherein the nonpolar liquid is miscible with the alcohol and compound of formula (1), but is immiscible with the ionic liquid, and wherein the nonpolar liquid is not reactive with the compound of formula (1) in the presence of the CO_2; and

separating the ionic liquid and the nonpolar liquid to isolate the nonpolar liquid.

2. A method for separating a nonpolar solute from a mixture, comprising:

providing a mixture comprising a nonpolar solute, water, a compound of formula (1), and CO_2, COS, CS_2 or a combination thereof, wherein the compound of formula (1) is:



(1)

where R^1, R^2, R^3, and R^4 are independently H; a substituted or unsubstituted C_1 to C_{10} alkyl group that is linear, branched, or cyclic; a substituted or unsubstiuted C_nSi_m group where n and m are independently a number from 0 to 10 and n+m is a number from 1 to 10; a substituted or unsubstituted aryl group optionally containing one or more {-Si(R^6)$_2$-O-} units; or a substituted or

unsubstituted heteroaryl group optionally containing one or more {-Si(R^6)$_2$-O-} units; R^6 is a substituted or unsubstituted alkyl, aryl, heteroaryl, or alkoxy moiety; and wherein the compound of formula (1) may be a monocyclic or bicyclic ring structure;

converting the water, the compound of formula (1), and the CO_2, COS, CS_2 or a combination thereof into an ionic liquid, wherein the nonpolar solute is miscible with the water and compound of formula (1), but is immiscible with the ionic liquid, and wherein the nonpolar solute is not reactive with the compound of formula (1) in the presence of the CO_2, COS, CS_2; and

separating the ionic liquid and nonpolar solute to isolate the nonpolar solute.

3. The method of claim 1, wherein the compound of formula (1) is added to a mixture of the nonpolar liquid and alcohol.

4. The method of claim 1, wherein the CO_2 is added to a mixture of the nonpolar liquid and alcohol.

5. The method of claim 1, wherein the mixture including the compound of formula (1) comprises an amount of amidine that is less than equimolar to the amount of alcohol so that after forming the ionic liquid, some alcohol remains.

6. The method of claim 1, wherein the mixture including the compound of formula (1) comprises an amount of amidine that is greater than equimolar to the amount of alcohol so that after forming the ionic liquid, some amidine remains in non-ionic form.

7. The method of claim 1, wherein the alcohol is R'OH, where R' is alkyl, alkenyl, alkynyl, aryl, silyl, or siloxyl, and may be linear, branched, or cyclic, and may be substituted or unsubstituted.

8. The method of claim 7, wherein substituent includes one or more of alkyl, alkenyl, alkynyl, aryl, aryl halide, heteroaryl, cyclyl, Si(alkyl)$_3$, Si(alkoxy)$_3$, halo, alkoxyl, amino, amide, hydroxyl, thioether, alkylcarbonyl, alkylcarbonyloxy, arylcarbonyloxy, alkoxycarbonyloxy, aryloxycarbonyloxy, carbonate, alkoxycarbonyl, aminocarbonyl, alkylthiocarbonyl, phosphate, phosphate ester, phosphonato, phosphinato, cyano, acylamino, imino, sulfhydryl, alkylthio, arylthio, thiocarboxylate, dithiocarboxylate, sulfate, sulfato, sulfamoyl, sulfonamide, nitro, nitrile, azido, heterocyclyl, ether, ester, silicon-containing moieties, thioester, and alkyl halide.

9. The method of claim 1, wherein the alcohol is a primary or a secondary alcohol.

10. The method of claim 1, wherein the ionic liquid can be converted to a mixture comprising the compound of formula (1) by heating the ionic liquid.

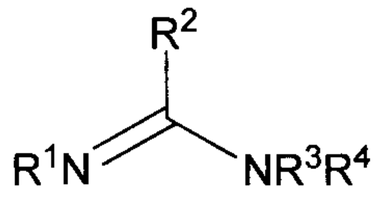
11. The method of claim 1, wherein the ionic liquid can be converted to a mixture comprising the compound of formula (1) by contacting the ionic liquid with a nonreactive gas that contains insufficient CO_2, COS or CS_2 to sustain the ionic liquid in its ionic form.

12. The method of claim 1, wherein the compound of formula (1) is 1,8 –diazabicyclo-[5.4.0]-undec-7-ene ("DBU").

13. The method of claim 1, wherein the alcohol is R'OH and the ionic liquid is $[DBUH]^+[ROCO_2]^-$ where R'OH is 1-propanol, 1-butanol, 1-hexanol, 1-octanol, 2-octanol, or 1-decanol.

14. A method for separating a nonpolar solute from a mixture, comprising:

providing a mixture comprising a nonpolar solute, an alcohol, a compound of formula (1), and CO_2, COS, CS_2 or a combination thereof, where the compound of formula (1) is:



(1)

where R^1, R^2, R^3, and R^4 are independently H; a substituted or unsubstituted C_1 to C_{10} alkyl group that is linear, branched or cyclic; a substituted or unsubstituted C_nSi_m group where n and m are independently a number from 0 to 10 and n+m is a number from 1 to 10; a substituted or unsubstituted aryl group optionally containing one or more $\{-Si(R^6)_2-O-\}$ units; or a substituted or unsubstituted heteroaryl group optionally containing one or more $\{-Si(R^6)_2-O-\}$ units; R^6 is a substituted or unsubstituted alkyl, aryl, heteroaryl, or alkoxy moiety; and wherein the compound of formula (1) may be a monocyclic or bicyclic ring structure;

converting the alcohol, the compound of formula (1), and the CO_2, COS, CS_2 or combination thereof into an ionic liquid, wherein the nonpolar solute is miscible with the alcohol and compound of formula (1), but is immiscible with the ionic liquid, and wherein the nonpolar solute is not reactive with the compound of formula (1) in the presence of the CO_2, COS, CS_2; and

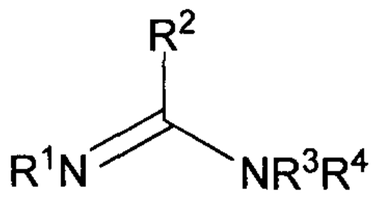
separating the ionic liquid and the nonpolar solute to isolate the nonpolar solute.

15. The method of claim 1, wherein the mixture further comprises a conventional solvent.

16. The method of claim 15, wherein the conventional solvent is toluene.

17. A method for separating a nonpolar liquid from a mixture, comprising:

providing a mixture comprising a nonpolar liquid, an alcohol, a compound of formula (1), and CO_2, COS, CS_2 or a combination thereof, wherein the compound of formula (1) is:



(1)

where R^1, R^2, R^3, and R^4 are independently H; a substituted or unsubstituted C_1 to C_{10} alkyl group that is linear, branched, or cyclic; a substituted or unsubstituted C_nSi_m group where n and m are independently a number from 0 to 10 and n+m is a number from 1 to 10; a substituted or unsubstituted aryl group optionally containing one or more {-Si(R^6)$_2$-O-} units; or a substituted or unsubstituted heteroaryl group optionally containing one or more {-Si(R^6)$_2$-O-} units; R^6 is a substituted or unsubstituted alkyl, aryl, heteroaryl, or alkoxy moiety; and wherein the compound of formula (1) may be a monocyclic or bicyclic ring structure;

converting the alcohol, the compound of formula (1), and the CO_2, COS, CS_2 or combination thereof into an ionic liquid, wherein the nonpolar liquid is miscible with the alcohol and compound of formula (1), but is immiscible with the ionic liquid, and wherein the nonpolar liquid is not reactive with the compound of formula (1) in the presence of the CO_2, COS, or CS_2; and

separating the ionic liquid and the nonpolar liquid to isolate the nonpolar liquid.

18. The method of claim 1, wherein the compound of formula (1) is a monocyclic or bicyclic ring structure.

19. The method of claim 18, wherein the compound of formula (1) is 1,8-diazabicyclo-[5.4.0]-undec-7-ene ("DBU").

20. The method of claim 14, wherein the compound of formula (1) is a monocyclic or bicyclic ring structure.

21. The method of claim 20, wherein the compound of formula (1) is 1,8-diazabicyclo-[5.4.0]-undec-7-ene ("DBU").

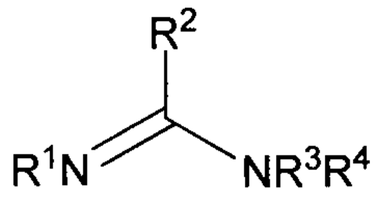
22. The method of claim 17, wherein the compound of formula (1) is a monocyclic or bicyclic ring structure.

23. The method of claim 22, wherein the compound of formula (1) is 1,8-diazabicyclo-[5.4.0]-undec-7-ene ("DBU").

24. The method of claim 2, wherein the compound of formula (1) is added to a mixture of water and the nonpolar solute.

25. A method for separating a nonpolar solute from a mixture, comprising:

providing a mixture comprising a nonpolar solute, a combination of alcohol and water, a compound of formula (1), and CO_2, COS, CS_2 or a combination thereof, wherein the compound of formula (1) is:



(1)

where R^1, R^2, R^3, and R^4 are independently H; a substituted or unsubstituted C_1 to C_{10} alkyl group that is linear, branched, or cyclic; a substituted or unsubstituted C_nSi_m group where n and m are independently a number from 0 to 10 and n+m is a number from 1 to 10; a substituted or unsubstituted aryl group optionally containing one or more {-Si(R^6)$_2$-O-} units; or a substituted or unsubstituted heteroaryl group optionally containing one or more {-Si(R^6)$_2$-O-} units; R^6 is a substituted or unsubstituted alkyl, aryl, heteroaryl, or alkoxy moiety; and wherein the compound of formula (1) may be a monocyclic or bicyclic ring structure;

converting the water, the alcohol, the compound of formula (1), and the CO_2, COS, CS_2 or combination thereof into an ionic liquid, wherein the nonpolar solute is miscible with the water, alcohol and compound of formula (1), but is immiscible with the ionic liquid, and wherein the

nonpolar solute is not reactive with the compound of formula (1) in the presence of the CO_2, COS, CS_2; and

separating the ionic liquid and the nonpolar solute to isolate the nonpolar solute.

26. The method of claim 25, wherein substituent includes one or more of alkyl, alkenyl, alkynyl, aryl, aryl halide, heteroaryl, cyclyl, $Si(alkyl)_3$, $Si(alkoxy)_3$, halo, alkoxyl, amino, amide, hydroxyl, thioether, alkylcarbonyl, alkylcarbonyloxy, arylcarbonyloxy, alkoxycarbonyloxy, aryloxycarbonyloxy, carbonate, alkoxycarbonyl, aminocarbonyl, alkylthiocarbonyl, phosphate, phosphate ester, phosphonato, phosphinato, cyano, acylamino, imino, sulfhydryl, alkylthio, arylthio, thiocarboxylate, dithiocarboxylate, sulfate, sulfato, sulfamoyl, sulfonamide, nitro, nitrile, azido, heterocyclyl, ether, ester, silicon-containing moieties, thioester, and alkyl halide.

27. The method of claim 25, wherein the ionic liquid can be converted to a mixture comprising the compound of formula (1) by heating the ionic liquid.

28. The method of claim 25, wherein the ionic liquid can be converted to a mixture comprising the compound of formula (1) by contacting the ionic liquid with a nonreactive gas that contains insufficient CO_2, COS, or CS_2 to sustain the ionic liquid in its ionic form.

29. The method of claim 1, wherein the alcohol is added to a mixture comprising the compound of formula (1) and the nonpolar liquid.

30. The method of claim 2, wherein the compound of formula (1) is a monocyclic or bicyclic ring structure.

31. The method of claim 30, wherein the compound of formula (1) is 1,8-diazabicyclo-[5.4.0]-undec-7-ene ("DBU").

32. The method of claim 25, wherein the compound of formula (1) is a monocyclic or bicyclic ring structure.

33. The method of claim 32, wherein the compound of formula (1) is 1,8-diazabicyclo-[5.4.0]-undec-7-ene ("DBU").

34. The method of claim 14, wherein the ionic liquid can be converted to a mixture comprising the compound of formula (1) by heating the ionic liquid.

35. The method of claim 14, wherein the ionic liquid can be converted to a mixture comprising the compound of formula (1) by contacting the ionic liquid with a nonreactive gas that contains insufficient CO_2, COS, or CS_2 to sustain the ionic liquid in its ionic form.

36. The method of claim 17, wherein the ionic liquid can be converted to a mixture comprising the compound of formula (1) by heating the ionic liquid.

37. The method of claim 17, wherein the ionic liquid can be converted to a mixture comprising the compound of formula (1) by contacting the ionic liquid with a nonreactive gas that contains insufficient CO_2, COS, or CS_2 to sustain the ionic liquid in its ionic form.

38. The method of claim 2, wherein the ionic liquid can be converted to a mixture comprising the compound of formula (1) by heating the ionic liquid.

39. The method of claim 2, wherein the ionic liquid can be converted to a mixture comprising the compound of formula (1) by contacting the ionic liquid with a nonreactive gas that contains insufficient CO_2, COS, or CS_2 to sustain the ionic liquid in its ionic form.

40. The method of any one of claims 1, 2, 14, 17, and 25, wherein R^1, R^3, and R^4 are not H.

41. A system for reversibly converting a non-ionic liquid to an ionic liquid, the system comprising:

(a) a non-ionic liquid mixture that comprises a switchable solvent comprising water and/or alcohol, and a basic, nitrogen-containing compound selected from the group consisting of:

(i) an amidine;

(ii) a guanidine; or

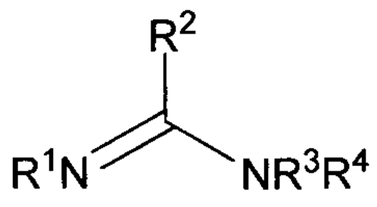
(iii) a combination of (i) and (ii); and

(b) means for contacting the non-ionic liquid mixture with CO_2 to convert the non-ionic liquid mixture to an ionic liquid mixture.

42. The system of claim 41, which additionally comprises means for removal of the CO_2 to convert the ionic liquid mixture to the non-ionic liquid mixture.

43. The system of claim 42, wherein the means for removal of the CO_2 comprises means for heating the ionic liquid mixture, means for contacting the ionic liquid mixture with a nonreactive gas that contains insufficient CO_2, CS_2, or COS to sustain the ionic liquid mixture in its ionic form, or both.

44. The system of claim 41, wherein the switchable solvent is amidine and alcohol; amidine and water; or amidine and alcohol and water; and the amidine is a compound of formula (1):



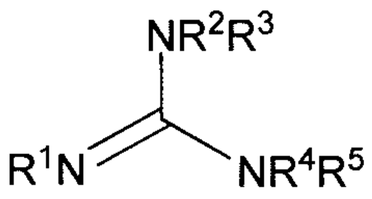
(1)

where R^1, R^2, R^3, and R^4 are independently H; a substituted or unsubstituted C_1 to C_{10} alkyl group that is linear, branched, or cyclic; a substituted or unsubstituted C_nSi_m group where n and m are independently a number from 0 to 10 and n + m is a number from 1 to 10; a substituted or unsubstituted aryl group optionally containing one or more {-Si(R^6)$_2$-O-} units; or a substituted or unsubstituted heteroaryl group optionally containing one or more {-Si(R^6)$_2$-O-} units; R^6 is a substituted or unsubstituted alkyl, aryl, heteroaryl, or alkoxy moiety; and wherein the compound of formula (1) may be a monocyclic or bicyclic ring structure.

45. The system of claim 44, wherein the compound of formula (1) is a monocyclic or bicyclic ring structure.

46. The system of claim 45, wherein the compound of formula (1) is 1,8-diazabicyclo-[5.4.0]-undec-7-ene ("DBU").

47. The system of claim 41, wherein the switchable solvent is guanidine and alcohol; guanidine and water; or guanidine and alcohol and water; and the guanidine is a compound of the formula (3):



(3)

where R^1, R^2, R^3, R^4, and R^5 are independently H; a substituted or unsubstituted C_1 to C_{10} alkyl group that is linear, branched, or cyclic; a substituted or unsubstituted C_nSi_m group where n and m are independently a number from 0 to 10 and n + m is a number from 1 to 10; a substituted or unsubstituted aryl group optionally containing one or more {-Si(R^6)$_2$-O-} units; or a substituted or unsubstituted heteroaryl group optionally containing one or more {-Si(R^6)$_2$-O-} units; R^6 is a substituted or unsubstituted alkyl, aryl, heteroaryl, or alkoxy moiety; and wherein the compound of formula (3) may be a monocyclic or bicyclic ring structure.

48. The system of claim 47, wherein the compound of formula (3) is a monocyclic or bicyclic ring structure.

49. The system of claim 41, wherein the switchable solvent is amidine and alcohol; amidine, alcohol and water; guanidine and alcohol; or guanidine, alcohol and water; and wherein the amidine or guanidine is in the same molecule as the alcohol.

50. The system of claim 41, which additionally comprises a conventional solvent.

51. A system for reversibly converting a non-ionic liquid to an ionic liquid, the system comprising:

(a) an ionic liquid mixture that comprises an ionized switchable solvent comprising water and/or alcohol, and a protonated, nitrogen-containing compound selected from the group consisting of:

(i) a protonated amidine;

(ii) a protonated guanidine; or

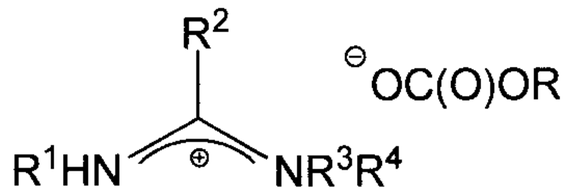
(iii) a combination of (i) and (ii);

(b) CO_2; and

(c) means for removal of the CO_2 to convert the ionic liquid mixture to a non-ionic liquid mixture.

52. The system of claim 51, wherein the means for removal of the CO_2 comprises means for heating the ionic liquid mixture, means for contacting the ionic liquid mixture with a nonreactive gas that contains insufficient CO_2, CS_2, or COS to sustain the ionic liquid mixture in its ionic form, or both.

53. The system of claim 51, wherein the ionized switchable solvent is protonated amidine and alcohol; protonated amidine and water; or protonated amidine and alcohol and water; and the protonated amidine is a compound of formula (2):



(2)

wherein

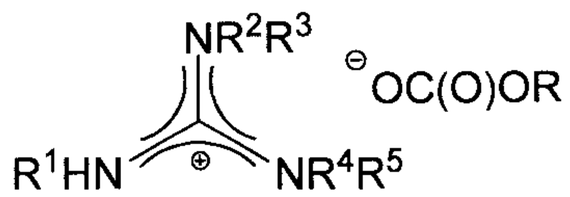
R is H, or R is alkyl, alkenyl, alkynyl, aryl, silyl, or siloxyl, and may be linear, branched, or cyclic, and may be substituted or unsubstituted;

R^1, R^2, R^3, and R^4 are independently H; a substituted or unsubstituted C_1 to C_{10} alkyl group that is linear, branched, or cyclic; a substituted or unsubstituted C_nSi_m group where n and m are independently a number from 0 to 10 and n + m is a number from 1 to 10; a substituted or unsubstituted aryl group optionally containing one or more {-Si(R^6)$_2$-O-} units; or a substituted or unsubstituted heteroaryl group optionally containing one or more {-Si(R^6)$_2$-O-} units; R^6 is a substituted or unsubstituted alkyl, aryl, heteroaryl, or alkoxy moiety; and wherein the compound of formula (2) may be a monocyclic or bicyclic ring structure.

54. The system of claim 53, wherein the compound of formula (2) is a monocyclic or bicyclic ring structure.

55. The system of claim 54, wherein the compound of formula (2) is protonated 1,8-diazabicyclo-[5.4.0]-undec-7-ene ("DBU H^+") $HOCO_2^-$.

56. The system of claim 51, wherein the ionized switchable solvent is protonated guanidine and alcohol; protonated guanidine and water; or protonated guanidine and alcohol and water; and the protonated guanidine is a compound of the formula (4):



(4)

wherein

R is H, or R is alkyl, alkenyl, alkynyl, aryl, silyl, or siloxyl, and may be linear, branched, or cyclic, and may be substituted or unsubstituted;

R^1, R^2, R^3, R^4, and R^5 are independently H; a substituted or unsubstituted C_1 to C_{10} alkyl group that is linear, branched, or cyclic; a substituted or unsubstituted C_nSi_m group where n and m are independently a number from 0 to 10 and n + m is a number from 1 to 10; a substituted or unsubstituted aryl group optionally containing one or more $\{-Si(R^6)_2-O-\}$ units; or a substituted or unsubstituted heteroaryl group optionally containing one or more $\{-Si(R^6)_2-O-\}$ units; R^6 is a substituted or unsubstituted alkyl, aryl, heteroaryl, or alkoxy moiety; and wherein the compound of formula (4) may be a monocyclic or bicyclic ring structure.

57. The system of claim 56, wherein the compound of formula (4) is a monocyclic or bicyclic ring structure.

58. The system of claim 51, wherein the ionized switchable solvent is protonated amidine and an alcohol; protonated amidine, alcohol and water; protonated guanidine and alcohol; or protonated guanidine, alcohol and water; and wherein the protonated amidine or protonated guanidine is in the same molecule as the alcohol.

59. The system of claim 51, which additionally comprises a conventional solvent.

60. The system of claim 44 or 53, wherein R^1, R^3, and R^4 are not H.

61. The system of claim 47 or 56, wherein R^1, R^2, R^3, R^4, and R^5 are not H.

62. A method of reversibly converting a non-ionic solvent to an ionic solvent, said method comprising contacting the non-ionic solvent with CO_2 to generate the ionic solvent, wherein the non-ionic solvent comprises a basic, nitrogen-containing compound and is selected from the group consisting of:

(i) an amidine and an alcohol;

(ii) an amidine and water;

(iii) an amidine, alcohol and water;

(iv) a guanidine and alcohol;

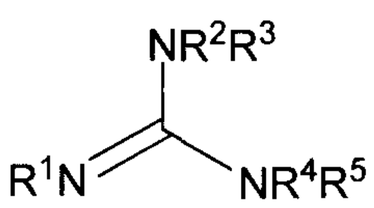
(v) a guanidine and water;

(vi) a guanidine, alcohol and water; and

(vii) any combination of (i) – (vi).

63. A method for separating a nonpolar liquid from a mixture, comprising:

providing a mixture comprising a nonpolar liquid, an alcohol, a compound of formula (3), and CO_2, where the compound of formula (3) is:



(3)

where R^1, R^2, R^3, R^4, and R^5 are independently H; a substituted or unsubstituted C_1 to C_{10} alkyl group that is linear, branched, or cyclic; a substituted or unsubstituted C_nSi_m group where n and m are independently a number from 0 to 10 and n + m is a number from 1 to 10; a substituted or unsubstituted aryl group optionally containing one or more {-Si(R^6)$_2$-O-} units; or a substituted or unsubstituted heteroaryl group optionally containing one or more {-Si(R^6)$_2$-O-} units; R^6 is a substituted or unsubstituted alkyl, aryl, heteroaryl, or alkoxy moiety; and wherein the compound of formula (3) may be a monocyclic or bicyclic ring structure;

converting the alcohol, the compound of formula (3), and the CO_2 into an ionic liquid, wherein the nonpolar liquid is miscible with the alcohol and compound of formula (3), but is immiscible with the ionic liquid, and wherein the nonpolar liquid is not reactive with the compound of formula (3) in the presence of the CO_2; and

separating the ionic liquid and the nonpolar liquid to isolate the nonpolar liquid.

64. The method of claim 63, wherein the compound of formula (3) is added to a mixture of the nonpolar liquid and alcohol.

65. The method of claim 63, wherein the CO_2 is added to a mixture of the nonpolar liquid and alcohol.

66. The method of claim 63, wherein the mixture including the compound of formula (3) comprises an amount of guanidine that is less than equimolar to the amount of alcohol so that after forming the ionic liquid, some alcohol remains.

67. The method of claim 63, wherein the mixture including the compound of formula (3) comprises an amount of guanidine that is greater than equimolar to the amount of alcohol so that after forming the ionic liquid, some guanidine remains in non-ionic form.

68. The method of claim 63, wherein the alcohol is R'OH, where R' is alkyl, alkenyl, alkynyl, aryl, silyl, or siloxyl, and may be linear, branched, or cyclic, and may be substituted or unsubstituted.

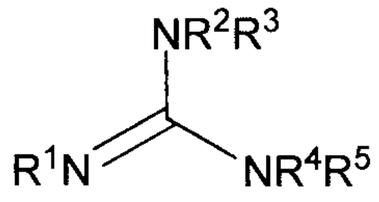
69. The method of claim 63, wherein the alcohol is a primary or a secondary alcohol.

70. The method of claim 63, wherein the mixture further comprises a conventional solvent.

71. The method of claim 63, wherein the alcohol is added to a mixture comprising the compound of formula (3) and the nonpolar liquid.

72. A method for separating a nonpolar solute from a mixture, comprising:

providing a mixture comprising a nonpolar solute, water, a compound of formula (3), and CO_2, COS, CS_2 or a combination thereof, wherein the compound of formula (3) is:



(3)

where R^1, R^2, R^3, R^4, and R^5 are independently H; a substituted or unsubstituted C_1 to C_{10} alkyl group that is linear, branched, or cyclic; a substituted or unsubstituted C_nSi_m group where n and m are independently a number from 0 to 10 and n + m is a number from 1 to 10; a substituted or unsubstituted aryl group optionally containing one or more {-Si(R^6)$_2$-O-} units; or a substituted or unsubstituted heteroaryl group optionally containing one or more {-Si(R^6)$_2$-O-} units; R^6 is a substituted or unsubstituted alkyl, aryl, heteroaryl, or alkoxy moiety; and wherein the compound of formula (3) may be a monocyclic or bicyclic ring structure;

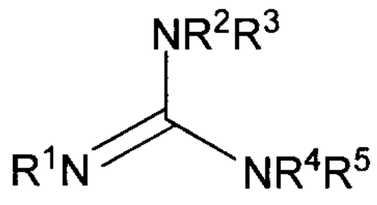
converting the water, the compound of formula (3), and the CO_2, COS, CS_2 or a combination thereof into an ionic liquid, wherein the nonpolar solute is miscible with the water and compound of formula (3), but is immiscible with the ionic liquid, and wherein the nonpolar solute is not reactive with the compound of formula (3) in the presence of the CO_2, COS, CS_2; and

separating the ionic liquid and nonpolar solute to isolate the nonpolar solute.

73. The method of claim 72, wherein the compound of formula (3) is added to a mixture of water and the nonpolar solute.

74. A method for separating a nonpolar solute from a mixture, comprising:

providing a mixture comprising a nonpolar solute, an alcohol, a compound of formula (3), and CO_2, COS, CS_2 or a combination thereof, where the compound of formula (3) is:



(3)

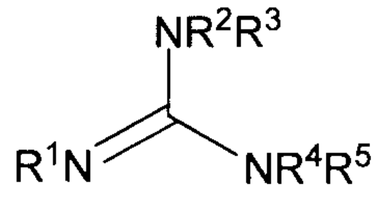
where R^1, R^2, R^3, R^4, and R^5 are independently H; a substituted or unsubstituted C_1 to C_{10} alkyl group that is linear, branched, or cyclic; a substituted or unsubstituted C_nSi_m group where n and m are independently a number from 0 to 10 and n + m is a number from 1 to 10; a substituted or unsubstituted aryl group optionally containing one or more {-Si(R^6)$_2$-O-} units; or a substituted or unsubstituted heteroaryl group optionally containing one or more {-Si(R^6)$_2$-O-} units; R^6 is a substituted or unsubstituted alkyl, aryl, heteroaryl, or alkoxy moiety; and wherein the compound of formula (3) may be a monocyclic or bicyclic ring structure;

converting the alcohol, the compound of formula (3), and the CO_2, COS, CS_2 or combination thereof into an ionic liquid, wherein the nonpolar solute is miscible with the alcohol and compound of formula (3), but is immiscible with the ionic liquid, and wherein the nonpolar solute is not reactive with the compound of formula (3) in the presence of the CO_2, COS, CS_2; and

separating the ionic liquid and the nonpolar solute to isolate the nonpolar solute.

75. A method for separating a nonpolar liquid from a mixture, comprising:

providing a mixture comprising a nonpolar liquid, an alcohol, a compound of formula (3), and CO_2, COS, CS_2 or a combination thereof, wherein the compound of formula (3) is:



(3)

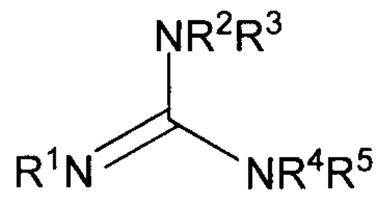
where R^1, R^2, R^3, R^4, and R^5 are independently H; a substituted or unsubstituted C_1 to C_{10} alkyl group that is linear, branched, or cyclic; a substituted or unsubstituted C_nSi_m group where n and m are independently a number from 0 to 10 and n + m is a number from 1 to 10; a substituted or unsubstituted aryl group optionally containing one or more {-Si(R^6)$_2$-O-} units; or a substituted or unsubstituted heteroaryl group optionally containing one or more {-Si(R^6)$_2$-O-} units; R^6 is a substituted or unsubstituted alkyl, aryl, heteroaryl, or alkoxy moiety; and wherein the compound of formula (3) may be a monocyclic or bicyclic ring structure;

converting the alcohol, the compound of formula (3), and the CO_2, COS, CS_2 or combination thereof into an ionic liquid, wherein the nonpolar liquid is miscible with the alcohol and compound of formula (3), but is immiscible with the ionic liquid, and wherein the nonpolar liquid is not reactive with the compound of formula (3) in the presence of the CO_2, COS, or CS_2; and

separating the ionic liquid and the nonpolar liquid to isolate the nonpolar liquid.

76. A method for separating a nonpolar solute from a mixture, comprising:

providing a mixture comprising a nonpolar solute, a combination of alcohol and water, a compound of formula (3), and CO_2, COS, CS_2 or a combination thereof, wherein the compound of formula (3) is:



(3)

where R^1, R^2, R^3, R^4, and R^5 are independently H; a substituted or unsubstituted C_1 to C_{10} alkyl group that is linear, branched, or cyclic; a substituted or unsubstituted C_nSi_m group where n and m are independently a number from 0 to 10 and n + m is a number from 1 to 10; a substituted or unsubstituted aryl group optionally containing one or more {-Si(R^6)$_2$-O-} units; or a substituted or unsubstituted heteroaryl group optionally containing one or more {-Si(R^6)$_2$-O-} units; R^6 is a substituted or unsubstituted alkyl, aryl, heteroaryl, or alkoxy moiety; and wherein the compound of formula (3) may be a monocyclic or bicyclic ring structure;

converting the water, the alcohol, the compound of formula (3), and the CO_2, COS, CS_2 or combination thereof into an ionic liquid, wherein the nonpolar solute is miscible with the water, alcohol and compound of formula (3), but is immiscible with the ionic liquid, and wherein the nonpolar solute is not reactive with the compound of formula (3) in the presence of the CO_2, COS, CS_2; and

separating the ionic liquid and the nonpolar solute to isolate the nonpolar solute.

77. The method of any one of claims 63 to 76, wherein substituent includes one or more of alkyl, alkenyl, alkynyl, aryl, aryl halide, heteroaryl, cyclyl, $Si(alkyl)_3$, $Si(alkoxy)_3$, halo, alkoxyl, amino, amide, hydroxyl, thioether, alkylcarbonyl, alkylcarbonyloxy, arylcarbonyloxy, alkoxycarbonyloxy, aryloxycarbonyloxy, carbonate, alkoxycarbonyl, aminocarbonyl, alkylthiocarbonyl, phosphate, phosphate ester, phosphonato, phosphinato, cyano, acylamino, imino, sulfhydryl, alkylthio, arylthio, thiocarboxylate, dithiocarboxylate, sulfate, sulfato, sulfamoyl, sulfonamide, nitro, nitrile, azido, heterocyclyl, ether, ester, silicon-containing moieties, thioester, and alkyl halide.

78. The method of any one of claims 63 to 76, wherein the ionic liquid can be converted to a mixture comprising the compound of formula (3) by heating the ionic liquid.

79. The method of any one of claims 63 to 76, wherein the ionic liquid can be converted to a mixture comprising the compound of formula (3) by contacting the ionic liquid with a nonreactive gas that contains insufficient CO_2, COS, or CS_2 to sustain the ionic liquid in its ionic form.

80. The method of any one of claims 63 to 79, wherein the compound of formula (3) is N,N,N',N'-tetramethyl-N"-butylguanidine.

81. The method of any one of claims 63 to 79, wherein the ionic liquid is N,N,N',N'-tetramethyl-N"-butylguanidinium methylcarbonate.

82. The method of any one of claims 63 to 79, wherein R^1, R^2, R^3, R^4, and R^5 are not H.

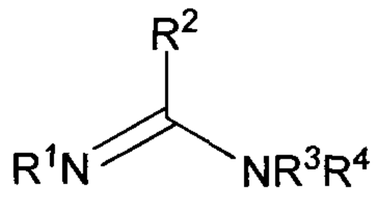
83. A composition comprising:

(a) CO_2 from a source other than air; and

(b) a switchable solvent formed by combining:

an amount of at least one R'OH, water, or a combination thereof, wherein R' is alkyl, alkenyl, alkynyl, aryl, silyl, or siloxyl, and may be linear, branched, or cyclic, and may be substituted or unsubstituted;

with an amount of a compound of formula (1)

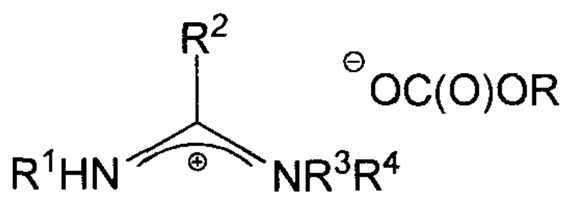


(1)

wherein

R^1, R^2, R^3, and R^4 are independently H; a substituted or unsubstituted C_1 to C_{10} alkyl group that is linear or branched; a substituted or unsubstituted C_3 to C_{10} cycloalkyl group; a substituted or unsubstituted C_nSi_m group where n and m are independently a number from 0 to 10 and n + m is a number from 1 to 10; a substituted or unsubstituted aryl group optionally containing one or more {-$Si(R^6)_2$-O-} units; or a substituted or unsubstituted heteroaryl group optionally containing one or more {-$Si(R^6)_2$-O-} units; R^6 is a substituted or unsubstituted alkyl, aryl, heteroaryl, or alkoxy moiety; and wherein the compound of formula (1) and the corresponding ionic liquid of formula (2) may be a monocyclic or bicyclic ring structure;

wherein the compound of formula (1) reversibly converts to an ionic liquid of formula (2)



(2) in the presence of the CO_2,

wherein R is H or R' as defined above, and R^1, R^2, R^3, and R^4 are as defined above; and wherein the amount of the compound of formula (1) is approximately equimolar to or greater than equimolar to the amount of the at least one R'OH, water, or combination thereof.

84. The composition of claim 83, wherein the CO_2 is gaseous and is present at a pressure of at least 1 atm.

85. The composition of claim 83, wherein the CO_2 is gaseous and is present at a pressure of greater than 1 atm.

86. The composition of claim 83, wherein R^1, R^3 and R^4 are not hydrogen.

87. The composition of claim 83, wherein the compound of formula (1) is a monocyclic or bicyclic ring structure.

88. The composition of claim 87, wherein the compound of formula (1) is 1,8-diazabicyclo-[5.4.0]-undec-7-ene ("DBU").

89. The composition of claim 83, wherein the ionic liquid of formula (2) is a monocyclic or bicyclic ring structure.

90. The composition of claim 89, wherein the ionic liquid of formula (2) is protonated 1,8-diazabicyclo-[5.4.0]-undec-7-ene ("$DBUH^+$") $HOCO_2^-$.

91. The composition of claim 83, wherein the at least one R'OH is a primary or a secondary alcohol.

92. The composition of claim 83, wherein one or more of R^1, R^2, R^3, and R^4 is substituted with hydroxyl.

93. The composition of claim 83, wherein R' is substituted with one or more of alkyl, alkenyl, alkynyl, aryl, aryl halide, heteroaryl, cyclyl, $Si(alkyl)_3$, $Si(alkoxy)_3$, halo, alkoxyl, amino, amide, hydroxyl, thioether, alkylcarbonyl, alkylcarbonyloxy, arylcarbonyloxy, alkoxycarbonyloxy, aryloxycarbonyloxy, carbonate, alkoxycarbonyl, aminocarbonyl, alkylthiocarbonyl, phosphate, phosphate ester, phosphonato, phosphinato, cyano, acylamino, imino, sulfhydryl, alkylthio, arylthio, thiocarboxylate, dithiocarboxylate, sulfate, sulfato, sulfamoyl, sulfonamide, nitro, nitrile, azido, heterocyclyl, ether, ester, silicon-containing moieties, thioester, and alkyl halide.

94. The composition of claim 83, wherein one or more of R^1, R^2, R^3, R^4, and R^6 is independently substituted with one or more of alkyl, alkenyl, alkynyl, aryl, aryl halide, heteroaryl, cyclyl, $Si(alkyl)_3$,

$Si(alkoxy)_3$, halo, alkoxyl, amino, amide, hydroxyl, thioether, alkylcarbonyl, alkylcarbonyloxy, arylcarbonyloxy, alkoxycarbonyloxy, aryloxycarbonyloxy, carbonate, alkoxycarbonyl, aminocarbonyl, alkylthiocarbonyl, phosphate, phosphate ester, phosphonato, phosphinato, cyano, acylamino, imino, sulfhydryl, alkylthio, arylthio, thiocarboxylate, dithiocarboxylate, sulfate, sulfato, sulfamoyl, sulfonamide, nitro, nitrile, azido, heterocyclyl, ether, ester, silicon-containing moieties, thioester, and alkyl halide.

95. The composition of claim 83, wherein the ionic liquid is $[DBUH]^+ [ROCO_2]^-$ where R is R' and the at least one R'OH comprises 1-propanol, 1-butanol, 1-hexanol, 1-octanol, 2-octanol, 1-decanol, or phenol.

96. The composition of claim 83, wherein the amount of the compound of formula (1) is approximately equimolar to the amount of the at least one R'OH, water or combination thereof.

97. The composition of claim 83, wherein the amount of the compound of formula (1) is greater than equimolar to the amount of the at least one R'OH, water or combination thereof.

98. The composition of claim 83, wherein R^1, R^2, R^3, and R^4 are independently a substituted or unsubstituted C_1 to C_4 alkyl group that is linear or branched.

99. The composition of claim 83, wherein R is H or alkyl.

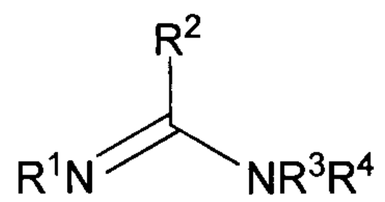
100. A composition comprising:

(a) CO_2 from a source other than air; and

(b) a switchable solvent formed by combining:

at least one R'OH, water, or a combination thereof, wherein R' is alkyl, alkenyl, alkynyl, aryl, silyl, or siloxyl, and may be linear, branched, or cyclic, and may be substituted or unsubstituted;

with a compound of formula (1)

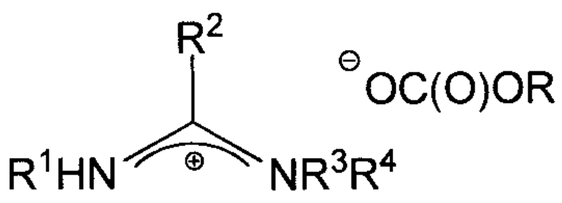


(1)

wherein

R^1, R^2, R^3, and R^4 are independently H; a substituted or unsubstituted C_1 to C_4 alkyl group that is linear or branched; a substituted or unsubstituted C_nSi_m group where n and m are independently a number from 0 to 4 and n + m is a number from 1 to 4; a substituted or unsubstituted C_3 or C_4 cycloalkyl group; or a substituted or unsubstituted heteroaryl group optionally containing one or more {-Si(R^6)$_2$-O-} units; R^6 is a substituted or unsubstituted alkyl, aryl, heteroaryl, or alkoxy moiety; and wherein the compound of formula (1) and the corresponding ionic liquid of formula (2) may be a monocyclic or bicyclic ring structure;

wherein the compound of formula (1) reversibly converts to an ionic liquid of formula (2)



(2) in the presence of the CO_2,

wherein R is H or R' as defined above, and R^1, R^2, R^3, and R^4 are as defined above.

101. The composition of claim 100, wherein the CO_2 is gaseous and is present at a pressure of at least 1 atm.

102. The composition of claim 100, wherein the CO_2 is gaseous and is present at a pressure of greater than 1 atm.

103. The composition of claim 100, wherein R^1, R^3 and R^4 are not hydrogen.

104. The composition of claim 100, wherein the compound of formula (1) is a monocyclic or bicyclic ring structure.

105. The composition of claim 104, wherein the compound of formula (1) is 1,8-diazabicyclo-[5.4.0]-undec-7-ene ("DBU").

106. The composition of claim 100, wherein the ionic liquid of formula (2) is a monocyclic or bicyclic ring structure.

107. The composition of claim 106, wherein the ionic liquid of formula (2) is protonated 1,8-diazabicyclo-[5.4.0]-undec-7-ene ("DBU H^+") $HOCO_2^-$.

108. The composition of claim 100, wherein the at least one R'OH is a primary or a secondary alcohol.

109. The composition of claim 100, wherein R' is substituted with one or more of alkyl, alkenyl, alkynyl, aryl, aryl halide, heteroaryl, cyclyl, $Si(alkyl)_3$, $Si(alkoxy)_3$, halo, alkoxyl, amino, amide, hydroxyl, thioether, alkylcarbonyl, alkylcarbonyloxy, arylcarbonyloxy, alkoxycarbonyloxy, aryloxycarbonyloxy, carbonate, alkoxycarbonyl, aminocarbonyl, alkylthiocarbonyl, phosphate, phosphate ester, phosphonato, phosphinato, cyano, acylamino, imino, sulfhydryl, alkylthio, arylthio, thiocarboxylate, dithiocarboxylate, sulfate, sulfato, sulfamoyl, sulfonamide, nitro, nitrile, azido, heterocyclyl, ether, ester, silicon-containing moieties, thioester, and alkyl halide.

110. The composition of claim 100, wherein one or more of R^1, R^2, R^3, R^4, and R^6 is independently substituted with one or more of heteroaryl, $Si(alkyl)_3$, $Si(alkoxy)_3$, halo, alkoxyl, amino, amide, hydroxyl, thioether, alkylcarbonyl, alkylcarbonyloxy, arylcarbonyloxy, alkoxycarbonyloxy, aryloxycarbonyloxy, carbonate, alkoxycarbonyl, aminocarbonyl, alkylthiocarbonyl, phosphate, phosphate ester, phosphonato, phosphinato, cyano, acylamino, imino, sulfhydryl, alkylthio, arylthio, thiocarboxylate, dithiocarboxylate, sulfate, sulfato, sulfamoyl, sulfonamide, nitro, nitrile, azido, heterocyclyl, ether, ester, thioester, and alkyl halide; and
substituents for R^6 include one or more of alkyl, alkenyl, alkynyl, aryl, aryl halide, heteroaryl, cyclyl, $Si(alkyl)_3$, $Si(alkoxy)_3$, halo, alkoxyl, amino, amide, hydroxyl, thioether, alkylcarbonyl, alkylcarbonyloxy, arylcarbonyloxy, alkoxycarbonyloxy, aryloxycarbonyloxy, carbonate, alkoxycarbonyl, aminocarbonyl, alkylthiocarbonyl, phosphate, phosphate ester, phosphonato, phosphinato, cyano, acylamino, imino, sulfhydryl, alkylthio, arylthio, thiocarboxylate, dithiocarboxylate, sulfate, sulfato, sulfamoyl, sulfonamide, nitro, nitrile, azido, heterocyclyl, ether, ester, silicon-containing moieties, thioester, and alkyl halide.

111. The composition of claim 110, wherein one or more of R^1, R^2, R^3, and R^4 is substituted with hydroxyl.

112. The composition of claim 100, wherein the ionic liquid is $[DBUH]^+$ $[ROCO_2]^-$ where R is R' and the at least one R'OH comprises 1-propanol, 1-butanol, 1-hexanol, 1-octanol, 2-octanol, 1-decanol, or phenol.

113. The composition of claim 100, wherein the compound of formula (1) and the at least one R'OH, water or combination thereof, are present in approximately equimolar amounts.

114. The composition of claim 100, wherein the compound of formula (1) is present at an amount that is less than equimolar to the amount present of the at least one R'OH, water or combination thereof.

115. The composition of claim 100, wherein the compound of formula (1) is present at an amount that is more than equimolar to the amount present of the at least one R'OH, water or combination thereof.

116. The composition of claim 100, wherein R^1, R^2, R^3, and R^4 are independently an unsubstituted C_1 to C_4 alkyl group that is linear or branched.

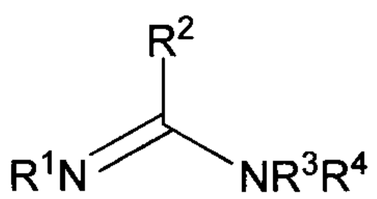
117. The composition of claim 100, wherein R is H or alkyl.

118. A composition comprising:

(a) CO_2 from a source other than air; and

(b) a switchable solvent having switchable polarity between a polar form and a nonpolar form, wherein said switchable solvent comprises:

at least one R'OH, water, or a combination thereof, wherein R' is alkyl, alkenyl, alkynyl, aryl, silyl, or siloxyl, and may be linear, branched, or cyclic, and may be substituted or unsubstituted; and a compound of formula (1)

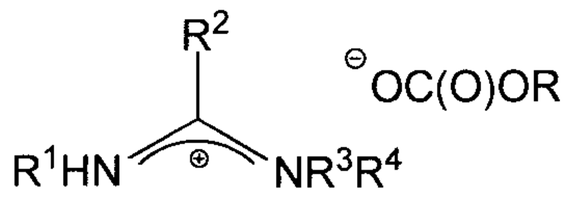


(1)

wherein

R^1, R^2, R^3, and R^4 are independently H; a substituted or unsubstituted C_1 to C_{10} alkyl group that is linear or branched; a substituted or unsubstituted C_3 to C_{10} cycloalkyl group; a substituted or unsubstituted C_nSi_m group where n and m are independently a number from 0 to 10 and n + m is a number from 1 to 10; a substituted or unsubstituted aryl group optionally containing one or more {-$Si(R^6)_2$-O-} units; or a substituted or unsubstituted heteroaryl group optionally containing one or more {-$Si(R^6)_2$-O-} units; R^6 is a substituted or unsubstituted alkyl, aryl, heteroaryl, or alkoxy moiety; and wherein the compound of formula (1) and the corresponding ionic liquid of formula (2) may be a monocyclic or bicyclic ring structure; and wherein, optionally, one of R^1, R^2, R^3, and R^4 combines with R' to connect the hydroxyl of the at least one R'OH as part of the compound of formula (1);

wherein the compound of formula (1) reversibly converts to an ionic liquid of formula (2)



(2)

in the presence of the CO_2,

wherein R is H or R' as defined above, and R^1, R^2, R^3, and R^4 are as defined above,

wherein the polarity of the switchable solvent is switched by the interconversion of the compound of formula (1) and the ionic liquid of formula (2).

119. The composition of claim 118, wherein the CO_2 is gaseous and is present at a pressure of at least 1 atm.

120. The composition of claim 118, wherein the CO_2 is gaseous and is present at a pressure of greater than 1 atm.

121. The composition of claim 118, wherein R^1, R^3 and R^4 are not hydrogen.

122. The composition of claim 118, wherein the compound of formula (1) is a monocyclic or bicyclic ring structure.

123. The composition of claim 122, wherein the compound of formula (1) is 1,8-diazabicyclo-[5.4.0]-undec-7-ene ("DBU").

124. The composition of claim 118, wherein the ionic liquid of formula (2) is a monocyclic or bicyclic ring structure.

125. The composition of claim 124, wherein the ionic liquid of formula (2) is protonated 1,8-diazabicyclo-[5.4.0]-undec-7-ene ("DBU H^+") $HOCO_2^-$.

126. The composition of claim 118, wherein the at least one R'OH is a primary or a secondary alcohol.

127. The composition of claim 118, wherein R' is substituted with one or more of alkyl, alkenyl, alkynyl, aryl, aryl halide, heteroaryl, cyclyl, $Si(alkyl)_3$, $Si(alkoxy)_3$, halo, alkoxyl, amino, amide, hydroxyl, thioether, alkylcarbonyl, alkylcarbonyloxy, arylcarbonyloxy, alkoxycarbonyloxy, aryloxycarbonyloxy, carbonate, alkoxycarbonyl, aminocarbonyl, alkylthiocarbonyl, phosphate, phosphate ester, phosphonato, phosphinato, cyano, acylamino, imino, sulfhydryl, alkylthio, arylthio, thiocarboxylate, dithiocarboxylate, sulfate, sulfato, sulfamoyl, sulfonamide, nitro, nitrile, azido, heterocyclyl, ether, ester, silicon-containing moieties, thioester, and alkyl halide.

128. The composition of claim 118, wherein one or more of R^1, R^2, R^3, R^4, and R^6 is independently substituted with one or more of alkyl, alkenyl, alkynyl, aryl, aryl halide, heteroaryl, cyclyl, $Si(alkyl)_3$, $Si(alkoxy)_3$, halo, alkoxyl, amino, amide, hydroxyl, thioether, alkylcarbonyl, alkylcarbonyloxy, arylcarbonyloxy, alkoxycarbonyloxy, aryloxycarbonyloxy, carbonate, alkoxycarbonyl, aminocarbonyl, alkylthiocarbonyl, phosphate, phosphate ester, phosphonato, phosphinato, cyano, acylamino, imino, sulfhydryl, alkylthio, arylthio, thiocarboxylate, dithiocarboxylate, sulfate, sulfato, sulfamoyl, sulfonamide, nitro, nitrile, azido, heterocyclyl, ether, ester, silicon-containing moieties, thioester, and alkyl halide.

129. The composition of claim 128, wherein one of R^1, R^2, R^3, and R^4 combines with R' to connect the hydroxyl of the at least one R'OH as part of the compound of formula (1).

130. The composition of claim 118, wherein the ionic liquid is $[DBUH]^+$ $[ROCO_2]^-$ where R is R' and the at least one R'OH comprises 1-propanol, 1-butanol, 1-hexanol, 1-octanol, 2-octanol, 1-decanol, or phenol.

131. The composition of claim 118, wherein the compound of formula (1) and the at least one R'OH, water or combination thereof, are present in approximately equimolar amounts.

132. The composition of claim 118, wherein the compound of formula (1) is present at an amount that is less than equimolar to the amount present of the at least one R'OH, water or combination thereof.

133. The composition of claim 118, wherein the compound of formula (1) is present at an amount that is more than equimolar to the amount present of the at least one R'OH, water or combination thereof.

134. The composition of claim 118, wherein R^1, R^2, R^3, and R^4 are independently a substituted or unsubstituted C_1 to C_4 alkyl group that is linear or branched.

135. The composition of claim 118, wherein R is H or alkyl.

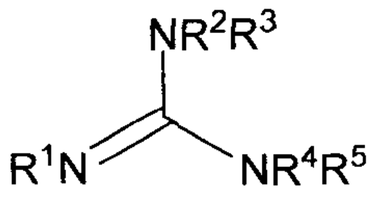
136. A composition comprising:

(a) CO_2 from a source other than air; and

(b) a switchable solvent formed by combining:

an amount of at least one R'OH, water, or a combination thereof, wherein R' is alkyl, alkenyl, alkynyl, aryl, silyl, or siloxyl, and may be linear, branched, or cyclic, and may be substituted or unsubstituted;

with an amount of a compound of formula (3)



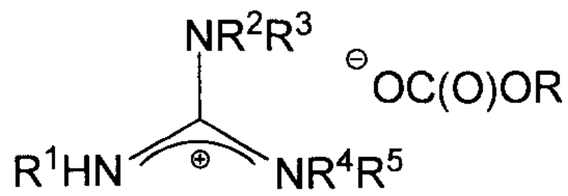
(3)

wherein

R^1, R^2, R^3, R^4, and R^5 are independently H; a substituted or unsubstituted C_1 to C_{10} alkyl group that is linear or branched; a substituted or unsubstituted C_3 to C_{10} cycloalkyl group; a substituted or unsubstituted C_nSi_m group where n and m are independently a number from 0 to 10 and n + m is a number from 1 to 10; a substituted or unsubstituted aryl group optionally containing one or more {-

$Si(R^6)_2$-O-} units; or a substituted or unsubstituted heteroaryl group optionally containing one or more {-$Si(R^6)_2$-O-} units; R^6 is a substituted or unsubstituted alkyl, aryl, heteroaryl, or alkoxy moiety; and wherein the compound of formula (3) and the corresponding ionic liquid of formula (4) may be a monocyclic or bicyclic ring structure;

wherein the compound of formula (3) reversibly converts to an ionic liquid of formula (4)



(4)

in the presence of the CO_2,

wherein R is H or R' as defined above, and R^1, R^2, R^3, R^4, and R^5 are as defined above; and

wherein the amount of the compound of formula (3) is approximately equimolar to or greater than equimolar to the amount of the at least one R'OH, water, or combination thereof.

137. The composition of claim 136, wherein the CO_2 is gaseous and is present at a pressure of at least 1 atm.

138. The composition of claim 136, wherein the CO_2 is gaseous and is present at a pressure of greater than 1 atm.

139. The composition of claim 136, wherein R^1, R^2, R^3, R^4, and R^5 are not hydrogen.

140. The composition of claim 136, wherein the at least one R'OH is a primary or a secondary alcohol.

141. The composition of claim 136, wherein one of more of R^1, R^2, R^3, R^4, and R^5 is substituted with hydroxyl.

142. The composition of claim 136, wherein R' is substituted with one or more of alkyl, alkenyl, alkynyl, aryl, aryl halide, heteroaryl, cyclyl, $Si(alkyl)_3$, $Si(alkoxy)_3$, halo, alkoxyl, amino, amide, hydroxyl, thioether, alkylcarbonyl, alkylcarbonyloxy, arylcarbonyloxy, alkoxycarbonyloxy, aryloxycarbonyloxy, carbonate, alkoxycarbonyl, aminocarbonyl, alkylthiocarbonyl, phosphate,

phosphate ester, phosphonato, phosphinato, cyano, acylamino, imino, sulfhydryl, alkylthio, arylthio, thiocarboxylate, dithiocarboxylate, sulfate, sulfato, sulfamoyl, sulfonamide, nitro, nitrile, azido, heterocyclyl, ether, ester, silicon-containing moieties, thioester, and alkyl halide.

143. The composition of claim 136, wherein one or more of R^1, R^2, R^3, R^4, R^5, and R^6 is independently substituted with one or more of alkyl, alkenyl, alkynyl, aryl, aryl halide, heteroaryl, cyclyl, $Si(alkyl)_3$, $Si(alkoxy)_3$, halo, alkoxyl, amino, amide, hydroxyl, thioether, alkylcarbonyl, alkylcarbonyloxy, arylcarbonyloxy, alkoxycarbonyloxy, aryloxycarbonyloxy, carbonate, alkoxycarbonyl, aminocarbonyl, alkylthiocarbonyl, phosphate, phosphate ester, phosphonato, phosphinato, cyano, acylamino, imino, sulfhydryl, alkylthio, arylthio, thiocarboxylate, dithiocarboxylate, sulfate, sulfato, sulfamoyl, sulfonamide, nitro, nitrile, azido, heterocyclyl, ether, ester, silicon-containing moieties, thioester, and alkyl halide.

144. The composition of claim 136, wherein the compound of formula (3) is N,N,N',N'-tetramethyl-N"-butylguanidine.

145. The composition of claim 136, wherein the ionic liquid of formula (4) is N,N,N',N'-tetramethyl-N"-butylguanidinium methylcarbonate.

146. The composition of claim 136, wherein the amount of the compound of formula (3) is approximately equimolar to the amount of the at least one R'OH, water or combination thereof.

147. The composition of claim 136, wherein the amount of the compound of formula (3) is greater than equimolar to the amount of the at least one R'OH, water or combination thereof.

148. The composition of claim 136, wherein R^1, R^2, R^3, R^4, and R^5 are independently a substituted or unsubstituted C_1 to C_4 alkyl group that is linear or branched.

149. The composition of claim 136, wherein R is H or alkyl.

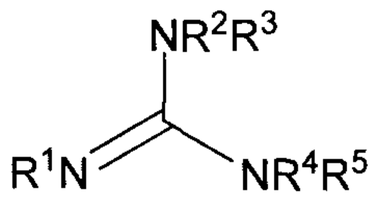
150. A composition comprising:

(a) CO_2 from a source other than air; and

(b) a switchable solvent formed by combining:

at least one R'OH, water, or a combination thereof, wherein R' is alkyl, alkenyl, alkynyl, aryl, silyl, or siloxyl, and may be linear, branched, or cyclic, and may be substituted or unsubstituted;

with a compound of formula (3)

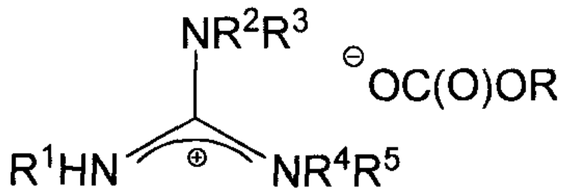


(3)

wherein

R^1, R^2, R^3, R^4, and R^5 are independently H; a substituted or unsubstituted C_1 to C_4 alkyl group that is linear or branched; a substituted or unsubstituted C_nSi_m group where n and m are independently a number from 0 to 4 and n + m is a number from 1 to 4; a substituted or unsubstituted C_3 or C_4 cycloalkyl group; or a substituted or unsubstituted heteroaryl group optionally containing one or more {-Si(R^6)$_2$-O-} units; R^6 is a substituted or unsubstituted alkyl, aryl, heteroaryl, or alkoxy moiety; and wherein the compound of formula (3) and the corresponding ionic liquid of formula (4) may be a monocyclic or bicyclic ring structure;

wherein the compound of formula (3) reversibly converts to an ionic liquid of formula (4)



(4)

in the presence of the CO_2,

wherein R is H or R' as defined above, and R^1, R^2, R^3, R^4, and R^5 are as defined above.

151. The composition of claim 150, wherein the CO_2 is gaseous and is present at a pressure of at least 1 atm.

152. The composition of claim 150, wherein the CO_2 is gaseous and is present at a pressure of greater than 1 atm.

153. The composition of claim 150, wherein R^1, R^2, R^3, R^4, and R^5 are not hydrogen.

154. The composition of claim 150, wherein the at least one R'OH is a primary or a secondary alcohol.

155. The composition of claim 150, wherein one of more of R^1, R^2, R^3, R^4, and R^5 is substituted with hydroxyl.

156. The composition of claim 150, wherein R' is substituted with one or more of alkyl, alkenyl, alkynyl, aryl, aryl halide, heteroaryl, cyclyl, $Si(alkyl)_3$, $Si(alkoxy)_3$, halo, alkoxyl, amino, amide, hydroxyl, thioether, alkylcarbonyl, alkylcarbonyloxy, arylcarbonyloxy, alkoxycarbonyloxy, aryloxycarbonyloxy, carbonate, alkoxycarbonyl, aminocarbonyl, alkylthiocarbonyl, phosphate, phosphate ester, phosphonato, phosphinato, cyano, acylamino, imino, sulfhydryl, alkylthio, arylthio, thiocarboxylate, dithiocarboxylate, sulfate, sulfato, sulfamoyl, sulfonamide, nitro, nitrile, azido, heterocyclyl, ether, ester, silicon-containing moieties, thioester, and alkyl halide.

157. The composition of claim 150, wherein one or more of R^1, R^2, R^3, R^4, R^5, and R^6 is independently substituted with one or more of heteroaryl, $Si(alkyl)_3$, $Si(alkoxy)_3$, halo, alkoxyl, amino, amide, hydroxyl, thioether, alkylcarbonyl, alkylcarbonyloxy, arylcarbonyloxy, alkoxycarbonyloxy, aryloxycarbonyloxy, carbonate, alkoxycarbonyl, aminocarbonyl, alkylthiocarbonyl, phosphate, phosphate ester, phosphonato, phosphinato, cyano, acylamino, imino, sulfhydryl, alkylthio, arylthio, thiocarboxylate, dithiocarboxylate, sulfate, sulfato, sulfamoyl, sulfonamide, nitro, nitrile, azido, heterocyclyl, ether, ester, thioester, and alkyl halide; and substituents for R^6 include one or more of alkyl, alkenyl, alkynyl, aryl, aryl halide, heteroaryl, cyclyl, $Si(alkyl)_3$, $Si(alkoxy)_3$, halo, alkoxyl, amino, amide, hydroxyl, thioether, alkylcarbonyl, alkylcarbonyloxy, arylcarbonyloxy, alkoxycarbonyloxy, aryloxycarbonyloxy, carbonate, alkoxycarbonyl, aminocarbonyl, alkylthiocarbonyl, phosphate, phosphate ester, phosphonato, phosphinato, cyano, acylamino, imino, sulfhydryl, alkylthio, arylthio, thiocarboxylate, dithiocarboxylate, sulfate, sulfato, sulfamoyl, sulfonamide, nitro, nitrile, azido, heterocyclyl, ether, ester, silicon-containing moieties, thioester, and alkyl halide.

158. The composition of claim 150, wherein the compound of formula (3) is N,N,N',N'-tetramethyl-N"-butylguanidine.

159. The composition of claim 150, wherein the ionic liquid of formula (4) is N,N,N',N'-tetramethyl-N"-butylguanidinium methylcarbonate.

160. The composition of claim 150, wherein the compound of formula (3) and the at least one R'OH, water or combination thereof, are present in approximately equimolar amounts.

161. The composition of claim 150, wherein the compound of formula (3) is present at an amount that is less than equimolar to the amount present of the at least one R'OH, water or combination thereof.

162. The composition of claim 150, wherein the compound of formula (3) is present at an amount that is more than equimolar to the amount present of the at least one R'OH, water or combination thereof.

163. The composition of claim 150, wherein R^1, R^2, R^3, R^4, and R^5 are independently an unsubstituted C_1 to C_4 alkyl group that is linear or branched.

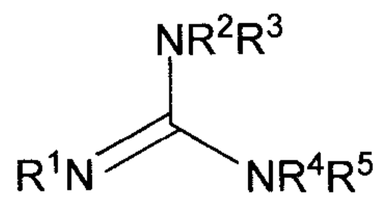
164. The composition of claim 150, wherein R is H or alkyl.

165. A composition comprising:

(a) CO_2 from a source other than air; and

(b) a switchable solvent having switchable polarity between a polar form and a nonpolar form, wherein said switchable solvent comprises:

at least one R'OH, water, or a combination thereof, wherein R' is alkyl, alkenyl, alkynyl, aryl, silyl, or siloxyl, and may be linear, branched, or cyclic, and may be substituted or unsubstituted; and a compound of formula (3)

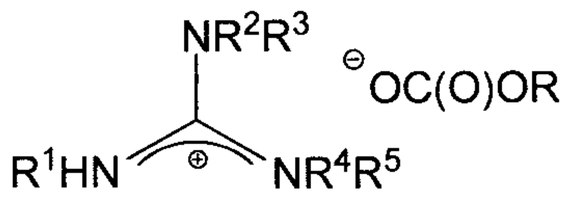


(3)

wherein

R^1, R^2, R^3, R^4, and R^5 are independently H; a substituted or unsubstituted C_1 to C_{10} alkyl group that is linear or branched; a substituted or unsubstituted C_3 to C_{10} cycloalkyl group; a substituted or unsubstituted C_nSi_m group where n and m are independently a number from 0 to 10 and n + m is a number from 1 to 10; a substituted or unsubstituted aryl group optionally containing one or more {-$Si(R^6)_2$-O-} units; or a substituted or unsubstituted heteroaryl group optionally containing one or more {-$Si(R^6)_2$-O-} units; R^6 is a substituted or unsubstituted alkyl, aryl, heteroaryl, or alkoxy moiety; and wherein the compound of formula (3) and the corresponding ionic liquid of formula (4) may be a monocyclic or bicyclic ring structure; and wherein, optionally, one of R^1, R^2, R^3, R^4, and R^5 combines with R' to connect the hydroxyl of the at least one R'OH as part of the compound of formula (3);

wherein the compound of formula (3) reversibly converts to an ionic liquid of formula (4)



(4)

in the presence of the CO_2,

wherein R is H or R' as defined above, and R^1, R^2, R^3, R^4, and R^5 are as defined above,

wherein the polarity of the switchable solvent is switched by the interconversion of the compound of formula (3) and the ionic liquid of formula (4).

166. The composition of claim 165, wherein the CO_2 is gaseous and is present at a pressure of at least 1 atm.

167. The composition of claim 165, wherein the CO_2 is gaseous and is present at a pressure of greater than 1 atm.

168. The composition of claim 165, wherein R^1, R^2, R^3, R^4, and R^5 are not hydrogen.

169. The composition of claim 165, wherein the at least one R'OH is a primary or a secondary alcohol.

170. The composition of claim 165, wherein R' is substituted with one or more of alkyl, alkenyl, alkynyl, aryl, aryl halide, heteroaryl, cyclyl, $Si(alkyl)_3$, $Si(alkoxy)_3$, halo, alkoxyl, amino, amide, hydroxyl, thioether, alkylcarbonyl, alkylcarbonyloxy, arylcarbonyloxy, alkoxycarbonyloxy,

aryloxycarbonyloxy, carbonate, alkoxycarbonyl, aminocarbonyl, alkylthiocarbonyl, phosphate, phosphate ester, phosphonato, phosphinato, cyano, acylamino, imino, sulfhydryl, alkylthio, arylthio, thiocarboxylate, dithiocarboxylate, sulfate, sulfato, sulfamoyl, sulfonamide, nitro, nitrile, azido, heterocyclyl, ether, ester, silicon-containing moieties, thioester, and alkyl halide.

171. The composition of claim 165, wherein one or more of R^1, R^2, R^3, R^4, and R^5 is independently substituted with one or more of alkyl, alkenyl, alkynyl, aryl, aryl halide, heteroaryl, cyclyl, $Si(alkyl)_3$, $Si(alkoxy)_3$, halo, alkoxyl, amino, amide, hydroxyl, thioether, alkylcarbonyl, alkylcarbonyloxy, arylcarbonyloxy, alkoxycarbonyloxy, aryloxycarbonyloxy, carbonate, alkoxycarbonyl, aminocarbonyl, alkylthiocarbonyl, phosphate, phosphate ester, phosphonato, phosphinato, cyano, acylamino, imino, sulfhydryl, alkylthio, arylthio, thiocarboxylate, dithiocarboxylate, sulfate, sulfato, sulfamoyl, sulfonamide, nitro, nitrile, azido, heterocyclyl, ether, ester, silicon-containing moieties, thioester, and alkyl halide.

172. The composition of claim 165, wherein one of R^1, R^2, R^3, R^4, and R^5 combines with R' to connect the hydroxyl of the at least one R'OH as part of the compound of formula (3).

173. The composition of claim 165, wherein the compound of formula (3) is N,N,N',N'-tetramethyl-N"-butylguanidine.

174. The composition of claim 165, wherein the ionic liquid of formula (4) is N,N,N',N'-tetramethyl-N"-butylguanidinium methylcarbonate.

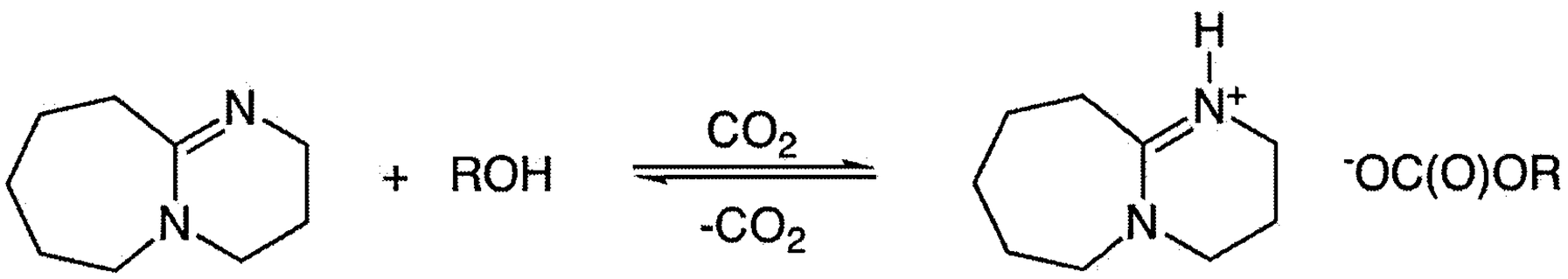
175. The composition of claim 165, wherein the compound of formula (3) and the at least one R'OH, water or combination thereof, are present in approximately equimolar amounts.

176. The composition of claim 165, wherein the compound of formula (3) is present at an amount that is less than equimolar to the amount present of the at least one R'OH, water or combination thereof.

177. The composition of claim 165, wherein the compound of formula (3) is present at an amount that is more than equimolar to the amount present of the at least one R'OH, water or combination thereof.

178. The composition of claim 165, wherein R^1, R^2, R^3, R^4, and R^5 are independently a substituted or unsubstituted C_1 to C_4 alkyl group that is linear or branched.

179. The composition of claim 165, wherein R is H or alkyl.


N
N
+ ROH
CO2
-CO2
H
N+
N
-OC(O)OR

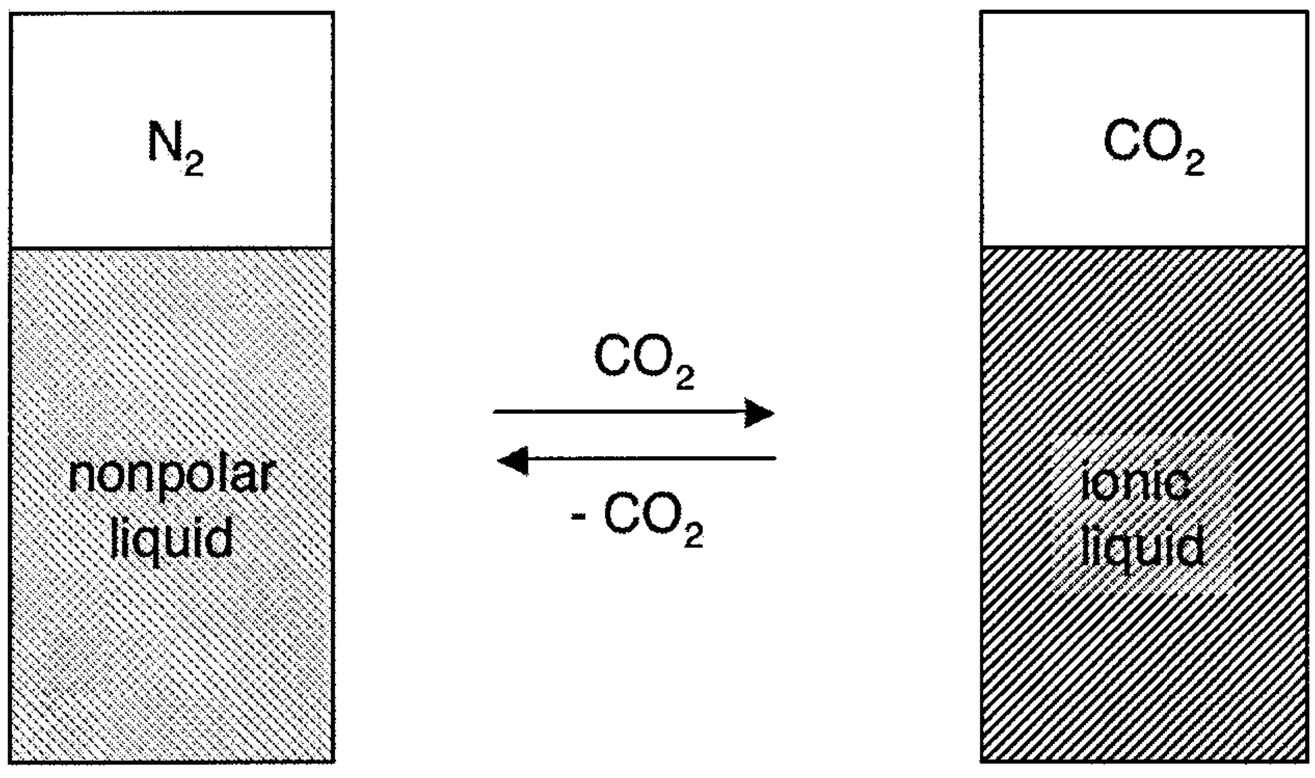

N2
nonpolar liquid
CO2
- CO2
CO2
ionic liquid

Figure 1

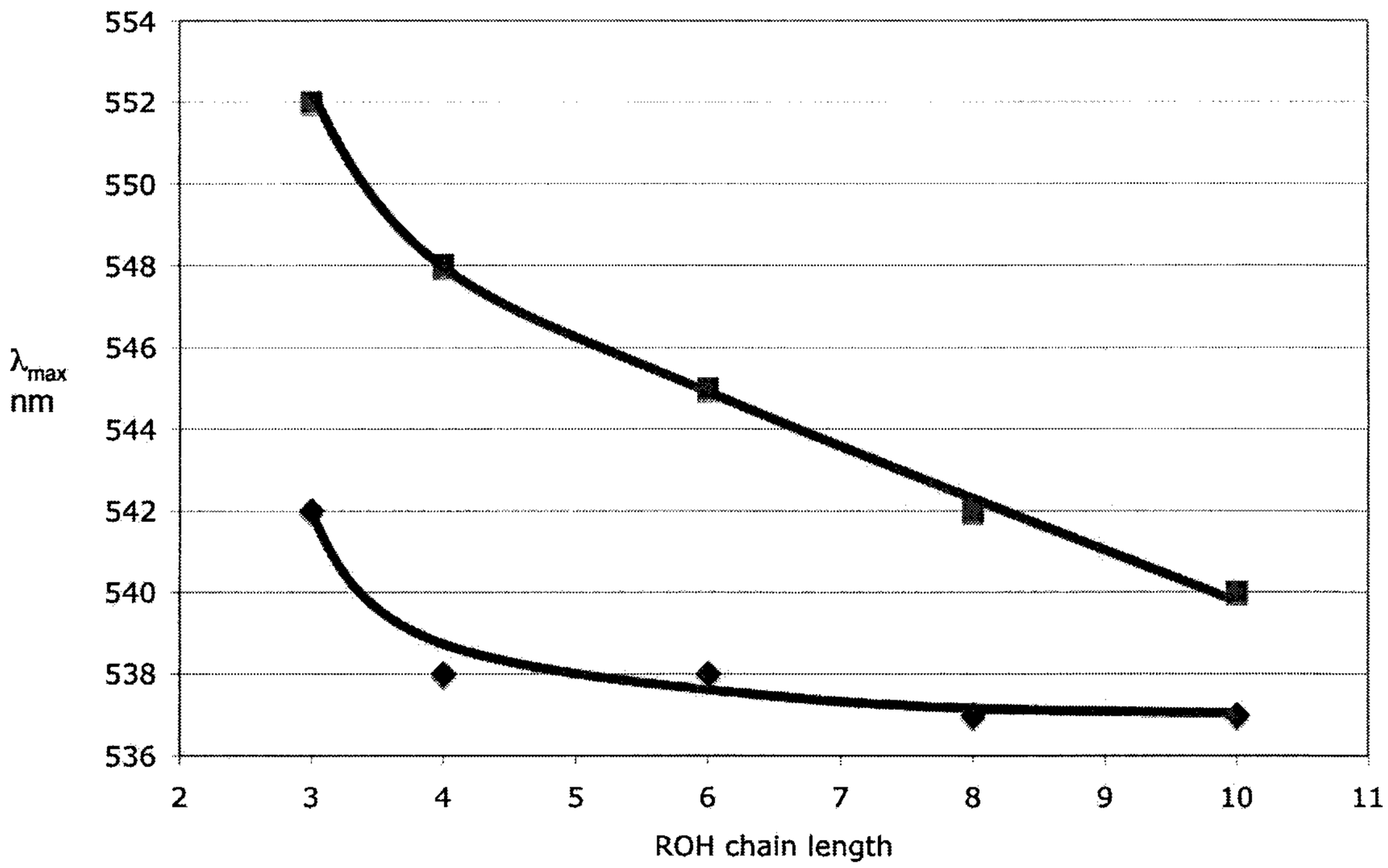


Figure 2

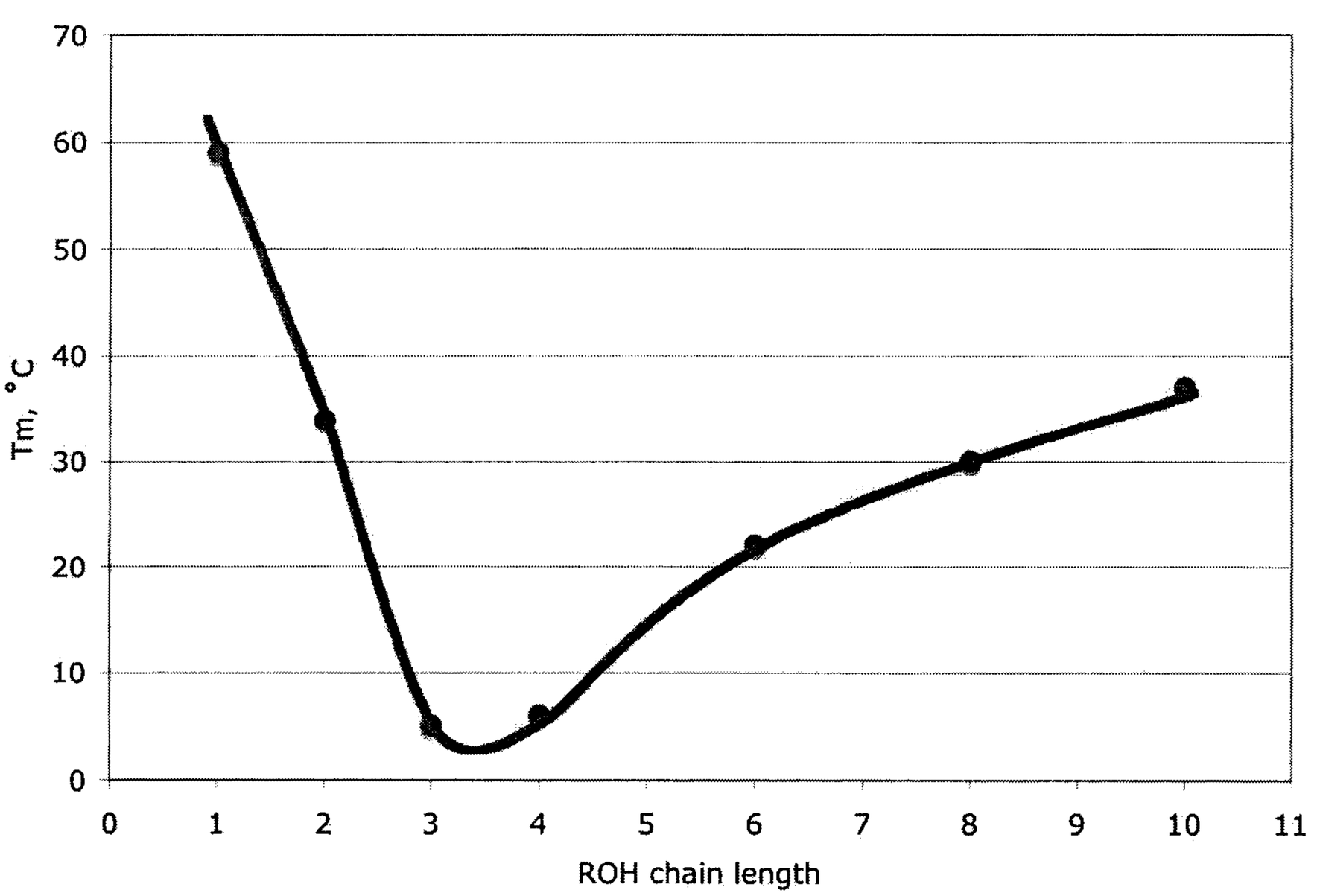


Figure 3

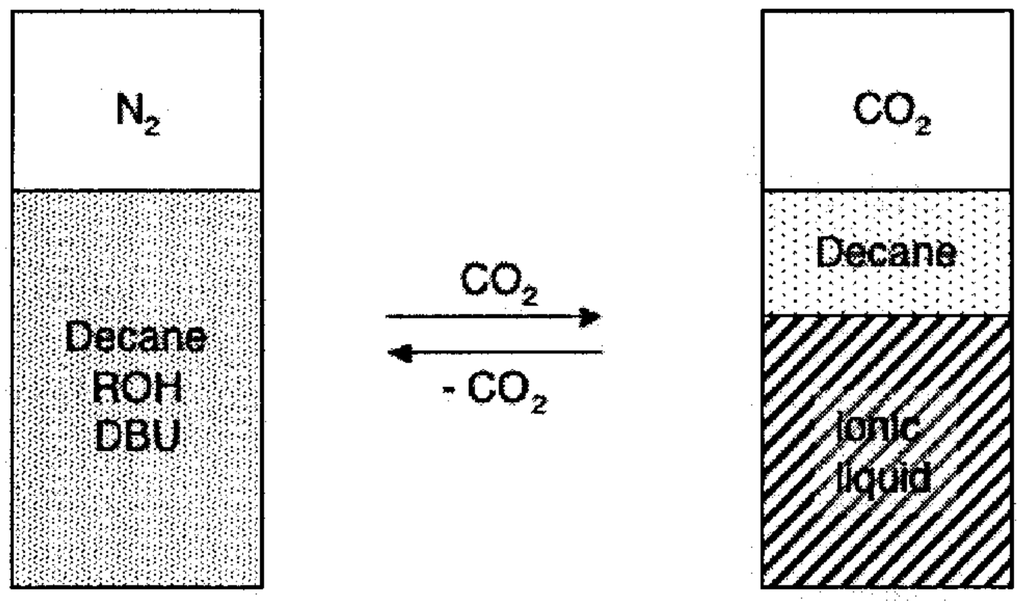


Figure 4

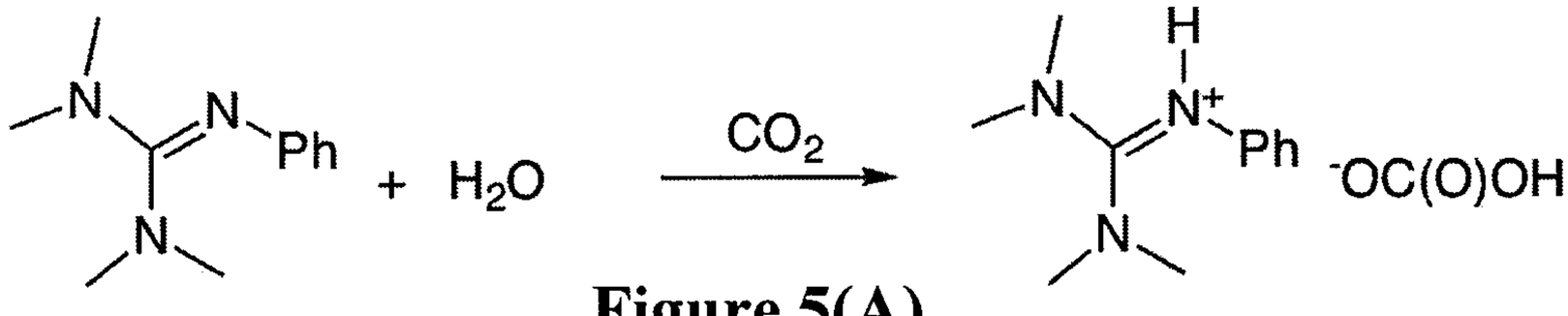


Figure 5(A)

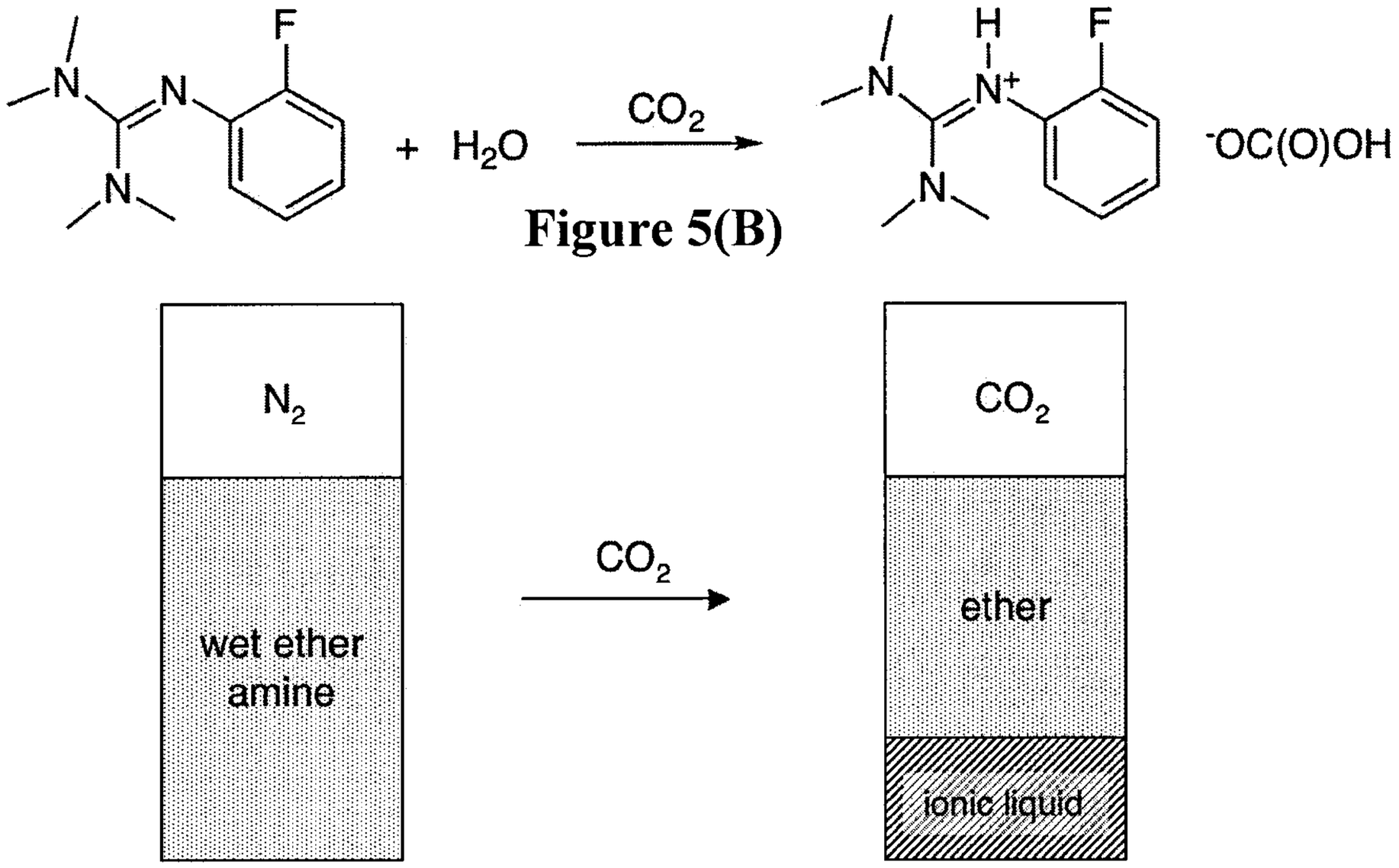


Figure 5(B)

Figure 5(C)

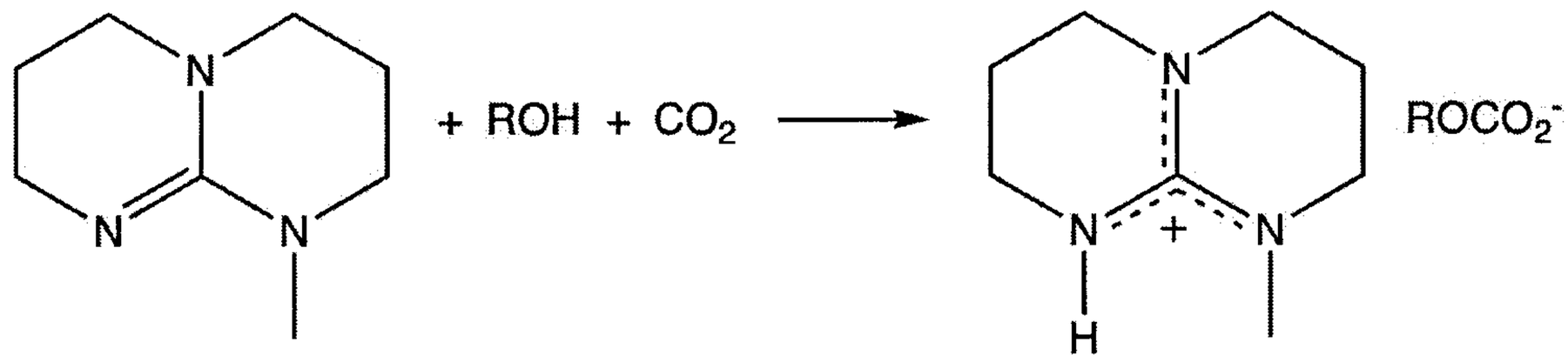


Figure 6(A)

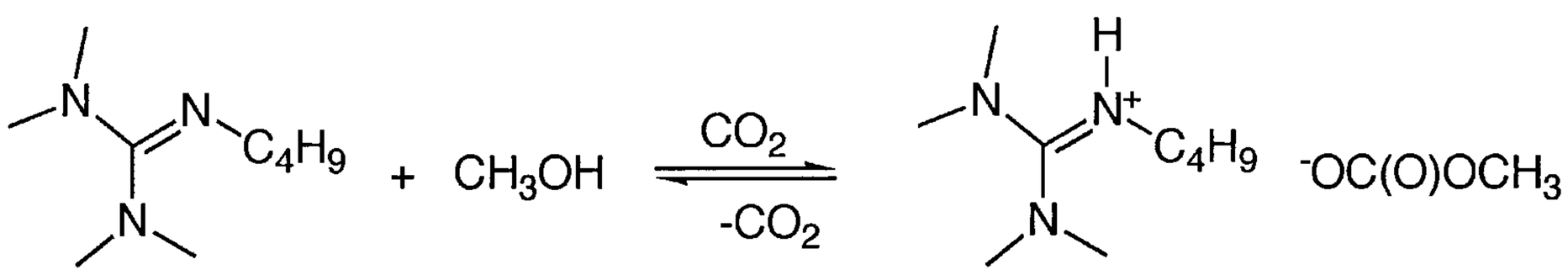
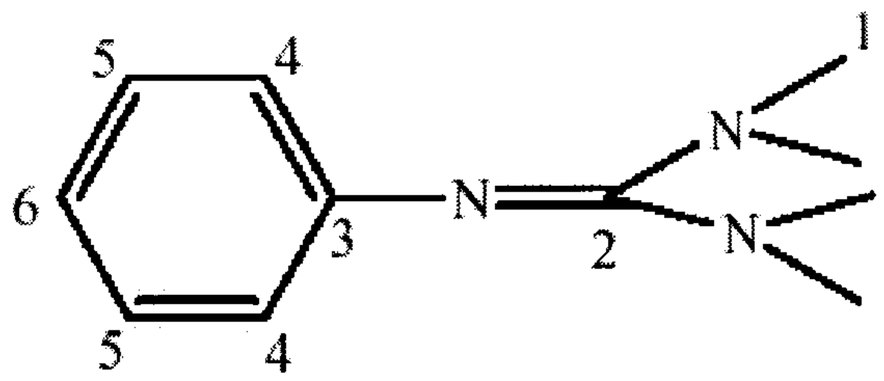


Figure 6(B)



^{1}H NMR chemical shifts of N,N,N',N'-tetramethyl-N"-phenylguanidine, its bicarbonate salt and HCl salt in $CDCl_3$[a]

Compound	H1	H4	H5	H6
tetramethylphenylguanidine	2.7	6.7	7.2	6.8 ppm
tetramethylphenylguanidinium bicarbonate salt	3.0	7.1	7.4	7.2
tetramethylphenylguanidinium hydrochloride salt	3.0	7.1	7.5	7.2

[a] H_1 appears as a singlet, H_4 as doublet and H_5 and H_6 as triplets.

^{13}C NMR chemical shifts (in ppm) of N,N,N',N'-tetramethyl-N"-phenylguanidine, its bicarbonate salt and HCl salt in $CDCl_3$

Compound Name	C_1	C_2	C_3	C_4	C_5	C_6
tetramethylphenylguanidine	39.8	162.7	152.2	121.4	130	122.3
tetramethylphenylguanidinium bicarbonate salt	39.9	159.5	138.8	121.3	130.3	125.7
tetramethylphenylguanidinium hydrochloride salt	40.8	160.5	139.8	122.7	131.8	127.3

Figure 7