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SECONDARY ALIPHATIC AMINES CONTAINING TERTIARY CARBON ATOMS

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16 Claims. (Cl. 260—583)

This invention concerns secondary aliphatic amines and a method for their preparation. These amines are characterized by unique properties that make them valuable in many hydrometallurgical applications for separating metals from aqueous solutions of their salts and for extracting mineral acids from aqueous systems.

The secondary aliphatic amines of the present invention may be represented by the formula



in which R is an alkyl or alkenyl group of 12 to 24 carbon atoms and R′ is an alkyl or alkenyl group of 12 to 24 carbon atoms. The alkyl and alkenyl representations of R must contain a tertiary carbon atom attached directly to the nitrogen atom, that is, in alpha position with respect to the nitrogen atom. These alkyl and alkenyl groups may also contain additional carbinyl carbon atoms and preferably so. The alkyl and alkenyl representations of R′ must contain at least one carbinyl carbon atom someplace in the group but it cannot be the carbon atom alpha or beta to the nitrogen atom. It is preferred that R be alkyl when R′ is alkenyl and that R′ be alkyl when R is alkenyl. The preferred arrangement is for R to be alkyl and R′ to be alkenyl. It is preferred that both R and R′ be highly branched.

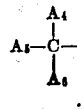
The definition of R may be more fully understood from the following formulas:

(1) When R is an alkyl group of 12 to 24 carbon atoms, R may be represented by



a trialkylcarbinyl group, in which A_1, A_2, and A_3 are alkyl groups having a total of 11 to 23 carbon atoms and

(2) When R is an alkenyl group of 12 to 24 carbon atoms, R may be represented by

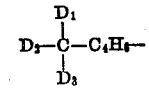


a dialkylalkenylcarbinyl group, in which A_4, A_5, and A_6 contain a total of 11 to 23 carbon atoms and one of them is an alkenyl group and the other two are alkyl groups.

It is to be understood that "carbinyl" is used to define a carbon atom having alkyl or alkenyl groups or both attached directly thereto, or an amino or halogen substituent with alkyl or alkenyl groups or both attached directly thereto but having no hydrogen atoms attached directly thereto. In the definition of R, the fourth valence of the carbinyl carbon is attached to the amino group.

The group R′ may be more fully understood from the following:

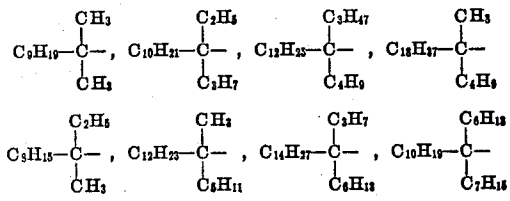
(1) When R′ is an alkenyl group of 12 to 24 carbon atoms, R′ may be represented by



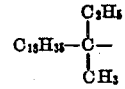
a trialkylcarbinylbutenyl group, in which D_1, D_2, and D_3 are alkyl groups containing a total of 7 to 19 carbon atoms and

(2) When R′ is an alkyl group is contains from 12 to 24 carbon atoms at least one of which is a carbinyl carbon. The term "carbinyl" is used in the definition of R′ in the same sense as it is used in the definition of R except that the fourth valence of the carbinyl carbon in the definition of R′ is attached to a butenylene group or to an alkylene as will be understood from the foregoing discussion. The groups A_1, A_2, A_3, A_4, A_5, A_6, D_1, D_2, and D_3 may contain carbinyl carbon atoms and it is desirable that, within any one reactant, R amine or R′ halide to be more fully described hereinafter, there be more than one carbinyl carbon atom.

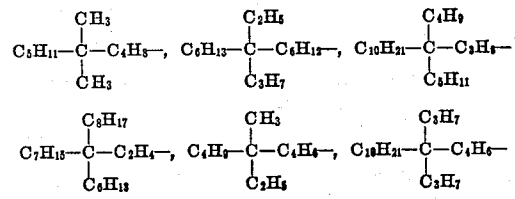
Typical of the R representations are

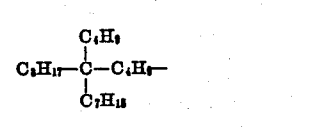


and

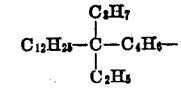


Typical of the R′ representations are





and



The present compounds are prepared by reacting an R amine with an R′ halide, such as chloride or bromide. It is advantageous to use, when possible, an alkenyl halide, such as a chloride or bromide, with an alkylamine, largely because the alkenyl halides used in this invention are somewhat more reactive than the alkyl halides.

Single compounds may be employed as reactants or mixtures of compounds may be used, as desired. Commercially available mixtures of trialkylcarbinylamines are particularly useful in thise respect as R amine reactants. Typical of these technical mixtures that may be employed are those containing from 12 to 15 carbon atoms and from 18 to 24 carbon atoms in amine form. One of the trialkylcarbinylbutenyl reactants that is of particular interest in the present instance is that identified as the 5,5,7,7-tetramethyl-2-octenyl group with a chlorine or bromine atom in the number one position.

The present secondary amines are formed by heating the reactants, already defined, at a reacting temperature in the range of about 75° to 200° C., preferably 120° to 180° C. The reaction is equimolecular in nature and yields greater than 75% and up to 95% or more are consistently obtained.

During the course of the reaction hydrogen halide is evolved and it is desirable to provide an alkaline hydrogen halide acceptor to remove the hydrogen halide, otherwise the reaction tends to become sluggish with yields appreciably reduced. There may be used in this respect solid sodium hydroxide, potassium hydroxide, calcium oxide, calcium hydroxide, barium hydroxide, and the like, or an excess of the amine reactant. If sodium hydroxide or its equivalent is employed, it is advantageous to supply a volatile, inert, organic solvent that forms an azeotrope with water, such as toluene, xylene, or the like, in order that the water formed by the neutralization reaction between the sodium hydroxide and the evolved hydrogen halide may be azeotropically removed as the reaction progresses. It is not necessary to supply the azeotropic solvent if an excess of the amine reactant is used as the hydrogen halide acceptor since there is no water by-product with which to cope. It is advantageous to employ an excess of the amine reactant as the hydrogen halide acceptor and in amounts such that substantially all of the evolved hydrogen halide is accepted. Since the present reaction occurs on an equimolecular basis and since a molar quantity of the amine reactant is used to accept the hydrogen halide formed, it is preferred to employ the amine reactant in a two to one molar ratio with the halide reactant when an excess of the amine reactant is used as the hydrogen halide acceptor.

If sodium hydroxide, potassium hydroxide or the like, is employed as the hydrogen halide acceptor, water is added to the reaction mixture, at the end of the reaction, to facilitate removal of the sodium or potassium halide salt formed as well as any excess alkali present. The water layer is easily separated from the organic layer containing the product. The organic layer is stripped preferably under reduced pressure to remove the solvent and any unused reactants. The product remains as the residue and may be distilled, if desired.

If an excess of the amine reactant is employed as the hydrogen halide acceptor, at the end of the reaction aqueous alkali is added to the reaction mixture and the resultant alkali halide salt formed is removed in the water layer along with any excess alkali. Any unused reactants are stripped off preferably under reduced pressure leaving the product as the residue which may be distilled, if desired. The products are viscous liquids that have the same approximate color as the amine reactants.

The subject compounds are insoluble in water and soluble in kerosene and other petroleum hydrocarbons, such as benzene, xylene, and toluene, common organic solvents, and light and heavy mineral oils. The present compounds are useful in many hydro-metallurgical applications wherein a kerosene or similar solution of one of the subject amines is agitated in an aqueous system containing the metal to be reclaimed or the metals to be separated. The present secondary amines exhibit extremely low emulsion tendencies and high extraction coefficients in many of these hydro-metallurgical systems. There may be separated from hydro-metallurgical systems in the above manner niobium from tantalum, niobium from protactinium, zinc from cobalt, uranium from its salts, and others, by employing the amines of this invention.

The subject amines are very useful for removing mineral acids, such as hydrochloric and sulfuric acids, from protein hydrolysates. These amines may also be employed to remove mineral acids such as hydrochloric and nitric acids from aqueous systems. For instance, employing a 0.1 N solution of the amine, whose preparation is shown in Example 1 to follow, in kerosene in an aqueous system containing 0.094 N hydrochloric acid 93.4% of the acid is removed when a two-to-one amine-to-acid ratio is used and 95.5% is removed when a three-to-one amine-to-acid ratio is employed. Using the same amine in the same concentration in kerosene in an aqueous system containing 0.1002 N nitric acid there is removed 97.5% of the acid when a two-to-one amine-to-acid ratio is used and 98.8% of the acid when a three-to-one amine-to-acid ratio is employed. Similar results are obtained by using the other amines of this invention. These amines are particularly useful in applications involving acid removal from aqueous systems because the amine salts formed are insoluble in water and, therefore, are easily removed from the water component. Furthermore, these amines are readily recovered by regeneration with sodium hydroxide, sodium carbonate, ammonium hydroxide, or the like, and are available for reuse. Under like conditions, dilaurylamine and other similar amines failed to produce the desired results. The dilaurylamine and other similar amine salts remained in the aqueous layer and appreciably aggravated the problem rather than solved it.

The secondary amines of this invention may also be employed as ashless detergents in lubricating oils, and, in amounts by weight in the range of about 0.0005 to 0.05%, are valuable as anti-sludging agents in fuel oils, burner oils, diesel fuel oils, and other cracked and straight run distillates normally tending to form sludge.

It is essential for the purposes of this invention that the present secondary amines contain the groups R and R′ as already defined in terms of molecular size and spatial configuration. Any appreciable deviation from the defined R and R′ groups defeats the purposes of this invention. By strict adherence to the defined groups, there results a concomitance of desirable properties that confers uniqueness on the compounds of this invention.

This application is a continuation-in-part of our application Serial No. 530,391, filed August 24, 1955, now abandoned.

The compounds of the present invention may be more fully understood from the following examples that are presented by way of illustration and not by way of limitation. Parts by weights are used throughout.

Example 1

There is added to a flask equipped with a thermometer and stirrer 223 parts of 1-chloro-5,5,7,7-tetramethyl-2-octene. A total of 396 parts of a mixture of trialkylcarbinylamines containing 12 to 15 carbon atoms, principally $C_{12}H_{25}NH_2$ and $C_{13}H_{27}NH_2$ and having a neutral equivalent of 191, is added over a period of one hour, during which time the temperature is maintained at 130° to 140° C. At the completion of the addition of the amine reactant, the temperature is raised to 180° C. for one hour. The reaction mixture is then neutralized by the addition of 40 parts of sodium hydroxide dissolved in 200 parts of water and heating the resultant mixture to 80° C. for one-half hour. The mixture is allowed to cool and separate into layers. The lower aqueous layer is discarded and the upper organic layer is stripped under reduced pressure using a small portion of benzene to assure the removal of all of the water. The stripped mixture is filtered hot and then distilled under reduced pressure. The product distills at 148° to 175° C. at 0.5 to 2.5 mm. of pressure. The product corresponds to a mixture of secondary amines in which the 5,5,7,7-tetramethyl-2-octenyl group is attached to the amino nitrogen of the trialkylcarbinylamine reactants.

In a similar way, a secondary amine of this invention is prepared by reacting 1-bromo-5,5,7,7-tetramethyl-2-octene with a mixture of trialkylcarbinylamine containing 18 to 24 carbon atoms, principally $C_{21}H_{43}NH_2$ and $C_{22}H_{45}NH_2$, and having a neutral equivalent of 320.

Example 2

There are introduced into a reaction vessel 202.5 parts

of 1-chloro-5,5,7,7-tetramethyl-2-octene and 706 parts of a trialkylcarbinylamine containing 24 carbon atoms. The reaction mixture is heated at 160° to 175° C. for two and a half hours. There is then added 56 parts of potassium hydroxide dissolved in 200 parts of water. The resultant mixture is heated to 75° C. and stirred for 40 minutes. The mixture is allowed to cool and separate into layers. The lower aqueous layer is discarded and the upper organic layer is stripped under reduced pressure. The stripped mixture is filtered hot leaving the product as the filtrate. The product corersponds to the secondary amine of this invention in which the 5,5,7,7-tetramethyl-2-octenyl group is attached to the amino nitrogen of the trialkylcarbinylamine reactant. The product may be named N-(5,5,7,7-tetramethyl-2-octenyl)-N-tetracosanylamine.

Example 3

There are brought together in a reaction vessel 286.5 parts of a trialkylcarbinylbutenyl chloride containing 18 carbon atoms and 702 parts of tricosylcarbinylamine. The mixture is heated for three hours at 170° to 175° C. and then 40 parts of sodium hydroxide dissolved in 175 parts of water is added. The mixture is stirred for 30 minutes at 75° C. and is then allowed to cool and separate into layers. The product is obtained as the residue from the upper organic layer after the layer has been stripped under reduced pressure. The product corresponds to the secondary amine of this invention which may be named N-octadecenyl-N-tetracosylamine.

There is prepared in like manner the secondary amine of this invention named N-odecyl-N-eicosylamine by reacting a trialkylcarbinylamine containing 12 carbon atoms with an eicosyl bromide containing a carbinyl atom further than alpha or beta away from the bromine atom.

In a similar way, there is made the secondary amine of this invention named N-tetracosyl-N-tetracosenylamine by reacting a trialkylcarbinylamine containing 24 carbon atoms with tetracosenyl chloride containing a carbinyl carbon atom further than alpha or beta away from the chlorine atom.

Example 4

There are added to a reaction vessel 213 parts of a trialkylcarbinylamine containing 14 carbon atoms, 40 parts of sodium hydroxide, and 50 parts of xylene. There is slowly added over a period of 40 minutes 286.5 parts of trialkylcarbinylbutenyl chloride having 18 carbon atoms while the temperature is maintained at 150° C. The reaction mixture is heated at 165° C. to 170° C. for four hours during which time water is distilled from the reaction vessel. The mixture is cooled, filtered, washed with water, and allowed to separate into layers. The organic layer is stripped leaving the product as the residue. The product corresponds to a secondary amine of this invention and may be named N-tetradecyl-N-octadecenylamine.

There is similarly prepared a secondary amine of this invention, which may be named N-hexadencyl-N-docosylamine, by reacting a trialkylcarbinylamine having 22 carbon atoms with a trialkylcarbinylbutenyl chloride having 16 carbon atoms.

We claim:

1. As a new composition of matter, the secondary amine having the formula



in which R is a member from the class consisting of alkyl and alkenyl groups of 12 to 24 carbon atoms and R' is a member from the class consisting of alkyl and alkenyl groups of 12 to 24 carbon atoms, said R group having a carbinyl carbon atom attached directly to the amino nitrogen atom and said R' group having at least one carbinyl carbon atom no one of which is closer than gamma with respect to the amino nitrogen atom.

2. As a new composition of matter, the secondary amine having the formula



in which R' is an alkenyl group of 12 to 24 carbon atoms containing at least one carbinyl carbon atom no one of which is closer than gamma with respect to the amino nitrogen atom and R is an alkyl group of 12 to 24 carbon atoms containing a carbinyl carbon atom attached directly to the amino nitrogen atom.

3. As a new composition of matter, the secondary amine having the formula



in which R is a trialkylcarbinyl group of 12 to 24 carbon atoms and R' is a trialkylcarbinylbutenyl group of 12 to 24 carbon atoms.

4. As a new composition of matter, the secondary amine having the formula



in which R' is a trialkylcarbinylbutenyl group of 12 to 24 carbon atoms and R is a trialkylcarbinyl group of 12 to 15 carbon atoms.

5. As a new composition of matter, the secondary amine having the formula



in which R' is a trialkylcarbinylbutenyl group of 12 to 24 carbon atoms and R is a trialkylcarbinyl group of 18 to 24 carbon atoms.

6. As a new composition of matter, the secondary amine having the formula



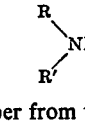
in which R' is the 5,5,7,7-tetramethyl-2-octenyl group and R is a trialkylcarbinyl group of 12 to 15 carbon atoms.

7. As a new composition of matter, the secondary amine having the formula



in which R' is the 5,5,7,7-tetramethyl-2-octenyl group and R is a trialkylcarbinyl group of 18 to 24 carbon atoms.

8. A method for the preparation of a secondary amine having the formula



in which R is a member from the class consisting of alkyl and alkenyl groups of 12 to 24 carbon atoms and R' is a member from the class consisting of alkyl and alkenyl groups of 12 to 24 carbon atoms, said R group having a carbinyl carbon atom attached directly to the amino nitrogen atom and said R' group having at least one carbinyl carbon atom no one of which is closer than gamma with respect to the amino nitrogen atom, which comprises heating in the presence of a hydrogen halide acceptor and at a reacting temperature in the range of about 75° to 200° C. and R amine with an R' halide, said halide

portion of the R′ reactant having an atomic weight of about 35.5 to 80.

9. A method for the preparation of a secondary amine having the formula



in which R is a member from the class consisting of alkyl and alkenyl groups of 12 to 24 carbon atoms and R′ is a member from the class consisting of alkyl and alkenyl groups of 12 to 24 carbon atoms, said R group having a carbinyl carbon atom attached directly to the amino nitrogen atom and said R′ group having at least one carbinyl carbon atom no one of which is closer than gamma with respect to the amino nitrogen atom, which comprises heating in the presence of an alkaline hydrogen halide acceptor from the class consisting of solid alkali metal and alkaline earth oxides and hydroxides in the presence of a volatile inert organic solvent that forms an azeotrope with water, and at a reacting temperature in the range of about 75° to 200° C. an R amine with an R′ halide, said halide portion of the R′ reactant having an atomic weight of about 35.5 to 80.

10. A method for the preparation of a secondary amine having the formula



in which R is a member from the class consisting of alkyl and alkenyl groups of 12 to 24 carbon atoms and R′ is a member from the class consisting of alkyl and alkenyl groups of 12 to 24 carbon atoms, said R group having a carbinyl carbon atom attached directly to the amino nitrogen atom and said R′ group having at least one carbinyl carbon atom no one of which is closer than gamma with respect to the amino nitrogen atom, which comprises heating at a reacting temperature in the range of about 75° to 200° C. an R amine with an R′ halide, said R amine being present in amounts approximately twice that of said R′ halide, said halide portion of the R′ reactant having an atomic weight of about 35.5 to 80.

11. A method for the preparation of a secondary amine having the formula



in which R′ is an alkenyl group of 12 to 24 carbon atoms containing at least one carbinyl carbon atom no one of which is closer than gamma to the amino nitrogen atom and R is an alkyl group of 12 to 24 carbon atoms containing a carbinyl carbon atom attached directly to the amino nitrogen atom, which comprises heating at a reacting temperature in the range of about 75° to 200° C. an R′ halide, in which the halide portion has an atomic weight of about 35.5 to 80, with an R amine.

12. A method for the preparation of a secondary amine having the formula



in which R is a trialkylcarbinyl group of 12 to 24 carbon atoms and R′ is a trialkylcarbinylbutenyl group of 12 to 24 carbon atoms, which comprises heating at a reacting temperature of about 75° to 200° C. an R′ halide, in which the halide portion has an atomic weight of about 35.5 to 80, with an R amine, said amine being present in amounts of approximately twice that of said halide.

13. A method for the preparation of a secondary amine having the formula

in which R′ is a trialkylcarbinylbutenyl group of 12 to 24 carbon atoms and R is a trialkylcarbinyl group of 12 to 15 carbon atoms, which comprises heating at a reacting temperature of about 75° to 200° C. an R′ halide, in which the halide portion has an atomic weight of about 35.5 to 80, with an R amine, said amine being present in amounts approximately twice that of said halide.

14. A method for the preparation of a secondary amine having the formula

in which R′ is a trialkylcarbinylbutenyl group of 12 to 24 carbon atoms and R is a trialkylcarbinyl group of 18 to 24 carbon atoms, which comprises heating at a reacting temperature of about 75° to 200° C. an R′ halide, in which the halide portion has an atomic weight of about 35.5 to 80, with an R amine, said amine being present in amounts approximately twice that of said halide.

15. A method for the preparation of a secondary amine having the formula

in which R′ is the 5,5,7,7-tetramethyl-2-octenyl group and R is a trialkylcarbinyl group of 12 to 15 carbon atoms, which comprises heating at a reacting temperature of about 75° to 200° C. an R′ halide, in which the halide portion has an atomic weight of about 35.5 to 80, with an R amine, said amine being present in amounts approximately twice that of said halide.

16. A method for the preparation of a secondary amine having the formula

in which R′ is the 5,5,7,7-tetramethyl-2-octenyl group and R is a trialkylcarbinyl group of 18 to 24 carbon atoms, which comprises heating at a reacting temperature of about 75° to 200° C. and R′ halide, in which the halide portion has an atomic weight of about 35.5 to 80, with an R amine, said amine being present in amounts approximately twice that of said halide.

No references cited.