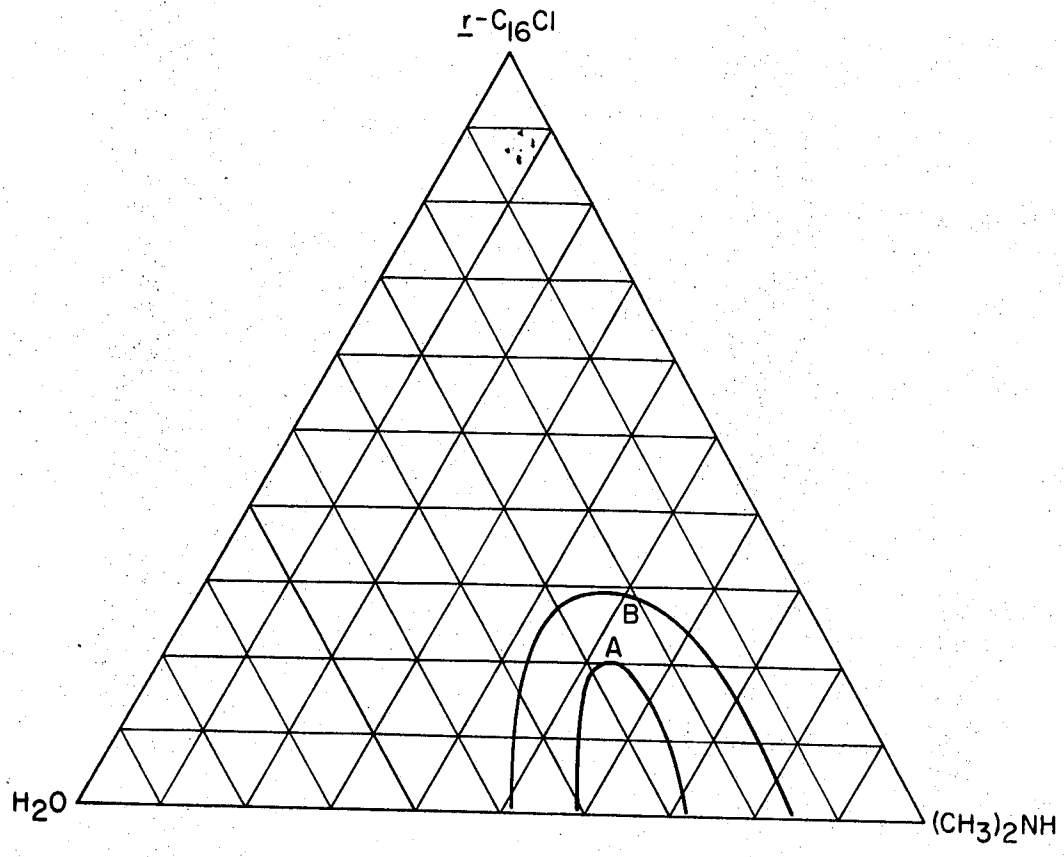
Nov. 24, 1970 T. L. BLANEY 3,542,876

AMINATION OF ALKYL HALIDES

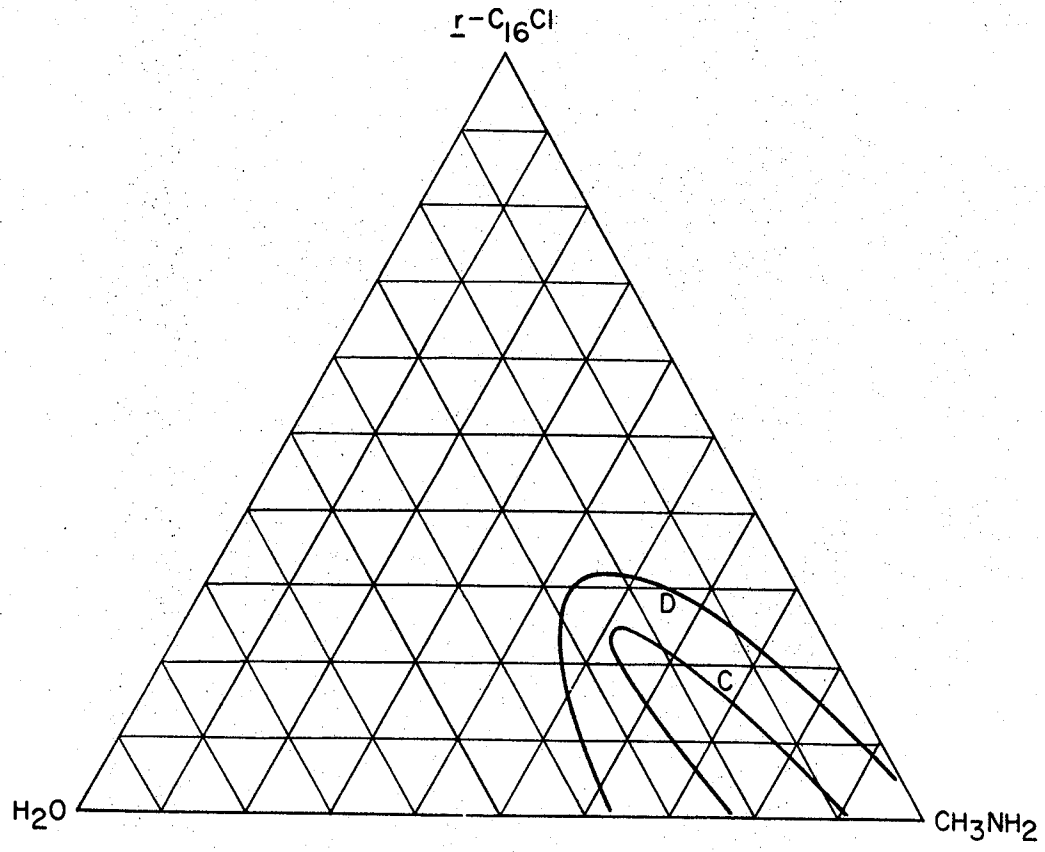
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Fig. 1



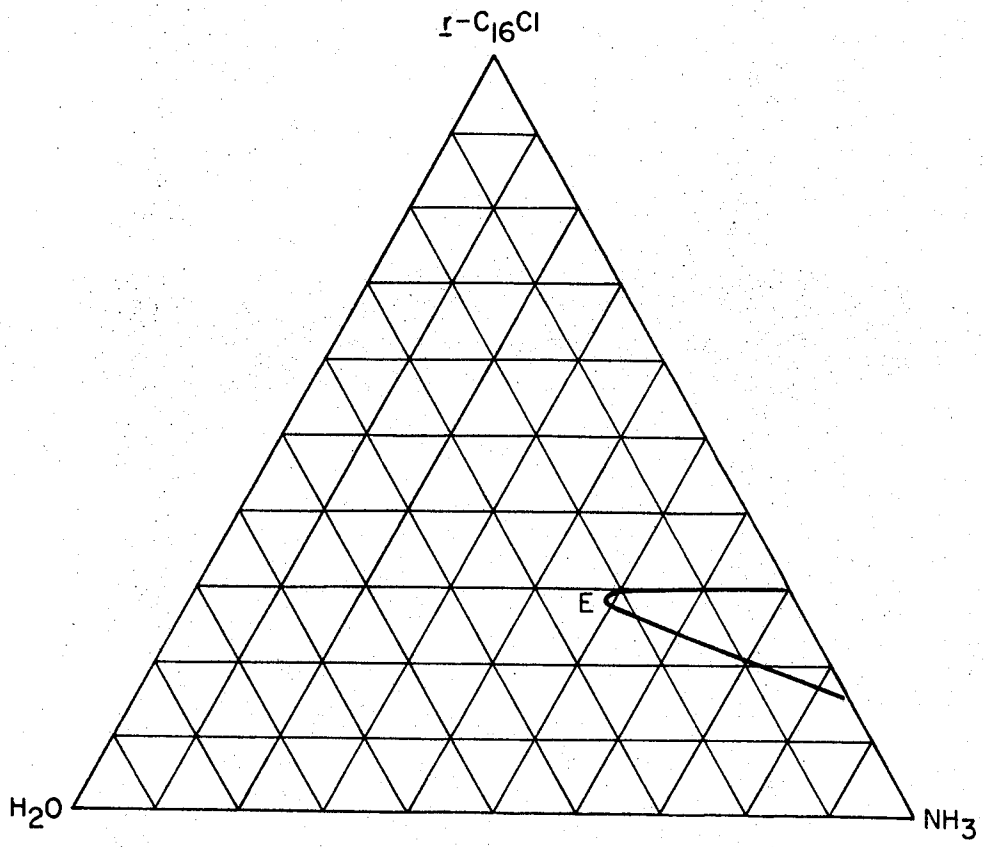
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Fig. 2



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Fig. 3



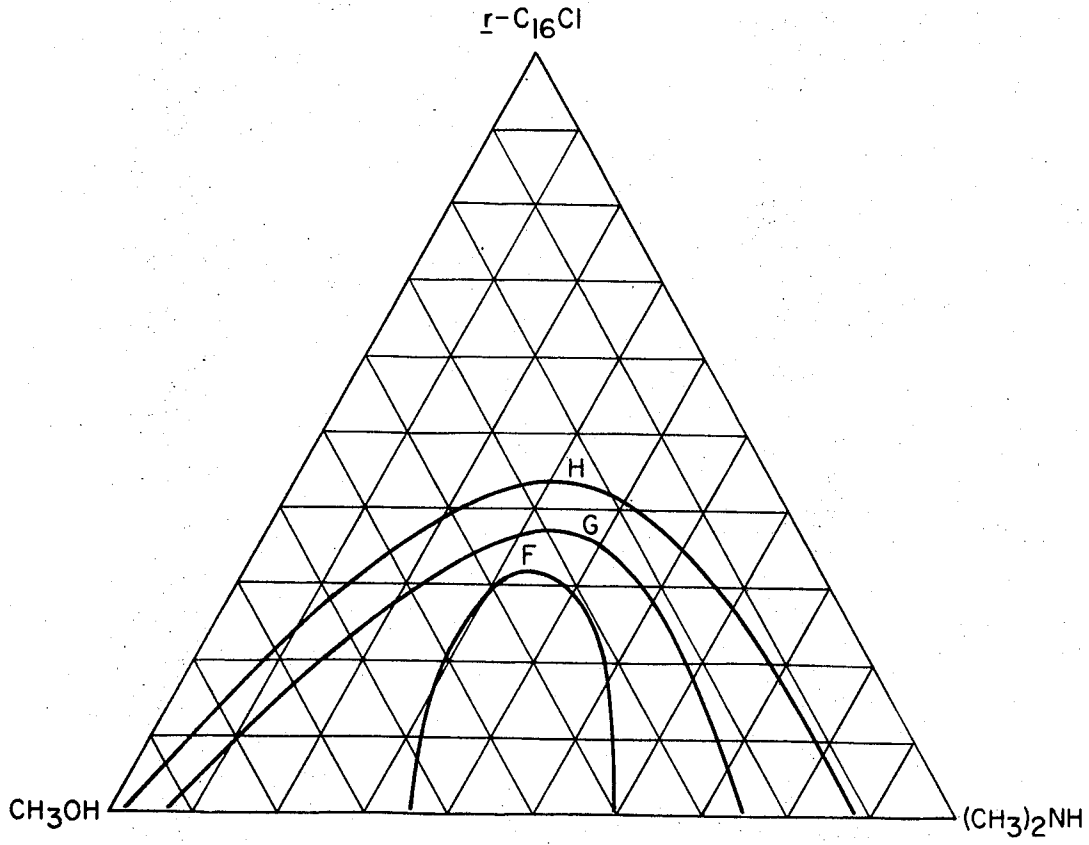
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AMINATION OF ALKYL HALIDES

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Fig. 4



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United States Patent Office 3,542,876 Patented Nov. 24, 1970

3,542,876

AMINATION OF ALKYL HALIDES

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Filed Sept. 26, 1968, Ser. No. 762,854
Int. Cl. C07c 85/04, 89/00
U.S. Cl. 260—583 6 Claims

ABSTRACT OF THE DISCLOSURE

A process for the amination of random alkyl halides is disclosed. A reaction mixture comprising a ternary system of a random alkyl halide, an amine base and a reaction medium (e.g., water, methanol and water/methanol mixtures) is prepared and heated to a reaction temperature of from about 150° F. to about 450° F. The products of this process, random alkyl primary, secondary and tertiary amines, are useful as intermediates in the production of synthetic detergents, fabric softening agents and bacteriostats.

FIELD OF THE INVENTION

This invention relates to amination of halogenated hydrocarbons and more particularly to amination of paraffin derived alkyl halides. In addition, this invention relates to the production of primary, secondary, and tertiary alkyl amines by the reaction of straight chain or branch chain alkyl halides with amine bases such as ammonia, primary amines, or secondary amines. This invention further relates to amination of internally halogenated paraffins heretofore thought to be too unreactive for commercial utilization in an amination reaction. Also this invention relates to a process whereby long chain alkyl internal primary, secondary and tertiary amines can be obtained in greatly improved yields and at greatly improved reaction rates over that heretofore obtainable.

PRIOR ART

Heretofore, aminated paraffin products have been obtained by aminating halogenated paraffin derivatives, obtained from halogenation of petroleum hydrocarbons. E. Profft in U.S. Pat. 2,305,830 discloses an amination process consisting of reacting chlorinated petroleum hydrocarbons with ammonia in alcohol or other solvents for four hours. R. L. Wakeman in U.S. Pat. 3,287,411 discloses an amination process, in which monochlorinated aliphatic hydrocarbons with the chlorine radical attached to the penultimate carbon atom are reacted with amines for six to seven hours. K. Keller in U.S. Pat. 1,948,924 discloses a process for the preparation of derivatives of paraffin hydrocarbons, containing at least 9 carbon atoms, by reacting ammonia (or an agent yielding ammonia, such as ammonium carbonate) with halogenated derivatives of paraffin hydrocarbons, containing at least 2 halogens, for two or three hours in an aqueous or alcoholic solution.

In the art hereinbefore cited, the processes all involve the reaction of an amine base, e.g., ammonia, a primary amine, or a secondary amine, with a halogenated paraffin in the presence of a solvent. However, in no instance is there a recognition nor an appreciation that the yields of the desired aminated reaction products and the reaction rates were critically dependent on the reactants used, the concentrations used or the reaction medium employed. Consequently, the processes described above involve the use of unreasonably long reaction times, and high temperatures and pressures.

The process of this invention represents a departure from the known prior art of aminating halogenated paraffins

by avoiding the necessity for using a specific type of halogenated hydrocarbon (e.g., a hydrocarbon having a terminal halide or a hydrocarbon having a halogen on the penultimate carbon atom) and using long reaction times (e.g. two to seven hours) at high reaction temperatures and pressures. In addition, the process of this invention reduces materially the formation of dialkyl amines which long has been a troublesome by-product in amination processes. The present invention provides an improved process for preparing alkyl amines, especially internal alkyl amines, in high yields according to a rapid and unique reaction. Reference is made to the accompanying drawings which are ternary diagrams illustrating the reaction mixture compositions used in the amination process described hereinafter in which the surprising and unexpected increase in yields and reaction rates are obtained.

DESCRIPTION OF THE INVENTION

The present invention in its broadest terms is a process which comprises reacting a random alkyl halide with an amine base in a reaction medium resulting in the displacement of the halogen atom by the amine base thereby forming a random alkyl amine and a hydrohalic acid. More specifically the process comprises preparing a reaction mixture consisting essentially of: (1) a random alkyl halide having the formula RX wherein R is a straight or branch chain alkyl radical containing from about 8 to about 24 carbon atoms, and wherein X is a halogen atom selected from the group consisting of chlorine, bromine and iodine, said halogen atom being randomly distributed on the alkyl chain; (2) an amine base having the formula

wherein R^1 and R^2 each are selected from the group consisting of hydrogen; alkyl groups having from 1 to about 3 carbon atoms; and hydroxyalkyl groups having from 1 to about 3 carbon atoms; and (3) a reaction medium selected from the group consisting of water, methanol, and mixtures thereof; and heating said reaction mixture to a temperature of from about 150° F. to about 450° F.

RANDOM ALKYL HALIDE

The random alkyl halide reactant useful for the present invention can be obtained by methods well-known in the art. (The term "random as used herein means that the halogen substituent can be located secondarily e.g., internally, at any position on the alkyl chain). For example, the random alkyl halides can be obtained from the hydrohalogenation of olefins, from direct halogenation of paraffins, or by other processes well known in the art for the production of alkyl halides. A distinct advantage and preferred embodiment of the process of this invention is that internally substituted halogens, e.g., halogens positioned internally on the carbon skeleton such as 4-chlorohexadecane, can be advantageously used. Heretofore, amination processes have almost exclusively used terminal halides and especially terminal bromides because of the greater reactivity of these species and the necessity for the use of these more reactive species in prior art processes.

The process of this invention is especially advantageous in aminating internal alkyl halides, so-called secondary and tertiary halides, because the process can be used to aminate these alkyl halides heretofore believed to be too unreactive for commercial utilization. Primary halides can also be aminated according to the process of this invention as well as in known prior art processes.

A common mthod of preparing alkyl halides is by hydrohalogenation of unsaturated paraffins. In the hydrohalogenation of unsaturated paraffins (i.e., the addition of a hydrogen halide to an olefin) the halogen substitutes

on the carbon atom of the double bond containing the least number of hydrogen atoms, in accordance with Markownikoffs rule. This provides feed stock containing predominately secondary halides and almost no primary halides. As is well known, terminal halogens can be displaced in an amination process much more readily than internal or secondary halogens, that is, halides substituted on a carbon atom other than on a terminal carbon atom. In addition, as is well known, halogens substituted on the second (penultimate) carbon are more readily displaced than those substituted more internally, i.e., on the third, fourth, etc., carbon atom. In addition, processes for the preparation of amines from halogenated paraffins have heretofore almost exclusively used primary alkyl bromides because the primary bromides provided even greater reactivity than the primary chlorides. Thus, heretofore halogenated paraffin feed stock which was to be reacted subsequently with amine bases according to processes well known in the art to obtain long chain amines were those with terminal or penultimate bromide substitution because of the necessity of using these more reactive species in prior art amination processes. Thus the prior art processes required that the halogenated paraffins be prepared using methods in which the halogen would be substituted in an anti-Markownikoff manner to obtain terminal halide substitution.

It was unexpected that the process of this invention could be advantageously employed to prepare amines by displacement of a halogen atom at any position in the carbon chain, e.g., any location on the alkyl chain, and any type of halogen atom, e.g., chloride, bromide and iodide, in view of the prior art.

As has been hereinbefore indicated in the process of this invention, the alkyl group of the random alkyl halide can be either branch chain or straight chain. In addition, mixtures of different alkyl chain lengths and halogens in different internal positions within the alkyl chain can be used. All of the halogens can be removed in the amination step of the present invention regardless of location in the chain. Thus, petroleum hydrocarbons which are halogenated directly by processes well known in the art to produce alkyl halides with the halogens substituted at any position can be used in the process of this invention. China lengths from about 8 carbon atoms to about 24 carbon atoms can be used. A preferred range is from about 10 carbon atoms to about 22 carbon atoms, since these chain length amines are of commercial interest in the production of synthetic detergents. For example, where alkyl halides having from about 10 to about 24 carbon atoms are reacted with dimethylamine and subsequently oxidized, using hydrogen peroxide, to the corresponding long chain amine oxides, the resulting amine oxides are useful as synthetic detergents in laundering textiles. The products of this process are also useful in the production of fabric softening compounds. For example, alkyl halides containing from about 16 to about 24 carbon atoms can be reacted with methylamine according to the process of this invention to produce secondary amines. These secondary amines can be then reacted with a primary halide to obtain tertiary amines which can be subsequently quaternized with methyl chloride. The resulting quaternary ammonium compounds are useful as fabric softening agents to be used in the rinse step in the laundering of textiles. In addition quaternary ammonium compounds are well known as bacteriostats. Alkyl halides having chain lengths shorter than about 8 carbon atoms can also be aminated by the procedure described herein. However, since these halides are relatively much more reactive than longer chain length halides, other conventional amination procedures can likewise be used with equally satisfactory results.

Examples of suitable random alkyl halides for the purposes of this invention which are illustrative and merely representative of the aforementioned classes are: straight chain secondary halogenated alkanes such as 2-chlorooctane, 3-chlorononance, 2-chlorodecane, 5-chloroundecane, 6-chlorododecane, 5-chlorotridecane, 7-chlorotetradecane, 5-chloropentadecane, 2-chlorohexadecane, 8-chloroheptadecane, 4-chlorooctadecane, 8-chlorononadecane, 10-chloroeicosane, and 10-chlorotetracosane, and mixtures thereof; 2-bromooctane, 3-bromononane, 2-bromodecane, 5-bromoundecane, 6-bromododecane, 6-bromotridecane, 7-bromotetradecane, 5-bromopentadecane, 2-bromohexadecane, 8-bromoheptadecane, 4-bromooctadecane, 8-bromononadecane, 4-bromoeicosane, 11-bromodocosane, and 12-bromotetracosane, and mixtures thereof; and 2-iodooctane, 3-iodononane, 5-iododecane, 5-iodoundecane, 6-iododododecane, 6-iodotridecane, 7-iodotetradecane, 5-iodopentadecane, 2-iodohexadecane, 7-iodoheptadecane, 3-iodooctadecane, 8-iodononadecane, 10-iodoeicosane, 11-iododocosane, and 4-iodotetracosane, and mixtures thereof. Specific examples of secondary branched chain alkyl halides which can be used in the process of this invention are 2-chloro-3-ethyldecane, 2-bromo-5-butyloctane, 2-iodo-5-ethyldodecane, 2-bromo-4-butyldecane, 2-bromo-3-hexyloctane, 4 - chloro - 2-ethyltetradecane, 12-chloro-5-butyldodecane, 2-bromo-6-hexyldecane, 3-chloro-5-methyldecane, 5 - chloro - 3 - propyloctane, 2-iodo-5-propyldodecane, 7 - bromo - 2-methyldecane, 6-chloro-4-ethylpentadecane, 14-chloro - 8-ethyldocosane, 7-iodo-2-octyldodecane, and 3-iodo-12-mthyldocosane. In addition tertiary halides, e.g., 2-methyl-2-chlorohexadecane, 5-ethyl-5 - bromoeicosane and 2,2 - dimethyl-10-ethyl-10-chlorodocosane, are also suitable for the process of this invention. As can be seen by the examples hereinbefore given, the location of the halogen atom can be at any of the carbons on the alkyl chain. The process of this invention is epecially advantageous in the use of secondary random alkyl halides. Mixtures of the chloro, bromo and iodo compounds can be used although this is not normally desired due to differences in relative reactivity and the difficulties encountered in commercial utilization of the process of this invention, e.g., where recycling the unreacted starting materials is desired. Straight chain halogenated paraffins or petroleums in which the halogens are chloro and bromo are preferred because of their availability and reactivity. Halogenated paraffins containing up to about 20% unhalogenated paraffin can also be used. The random alkyl chlorides, e.g., the chlorinated paraffins, are especially preferred because of their lower cost.

AMINE BASE

The term amine base as used in the description of this invention is used generically to describe ammonia, primary amines and secondary amines. The amine base acts as an attacking species to the halogen atom on the carbon skeleton.

The amine bases which can be used in the process of this invention have the formula

wherein R^1 and R^2 each are selected from the group consisting of hydrogen; alkyl groups having from 1 to about 3 carbon atoms; and hydroxyalkyl groups having from 1 to about 3 carbon atoms.

Where R^1 and R^2 are alkyl groups, suitable alkyl groups are as follows: methyl, ethyl, propyl, and iso-propyl. Where R^1 and R^2 are hydroxyalkyl groups, suitable groups are as follows: hydroxymethyl, hydroxyethyl, and hydroxypropyl. Straight chain alkyl groups are preferred. Methyl and ethyl are especially preferred.

Where both R^1 and R^2 are hydrogen, the amine base is ammonia.

Where the amine base is a primary amine, e.g., where R^1 is an alkyl or hydroxyalkyl group, and R^2 is hydrogen, illustrative amines are as follows: methylamine, ethylamine, propylamine, isopropylamine, 2 - hydroxyethylamine, and 3-hydroxypropylamine. Methylamine and ethylamine are preferred.

Where the amine base is a secondary amine, e.g., where both R^1 and R^2 are alkyl or hydroxyalkyl groups, illustrative amines are as follows: dimethylamine, ethylmethylamine, diethylamine, ethylpropylamine, and hydroxyethylmethylamine.

REACTION MEDIUM

It has now been discovered that the reaction between the random alkyl halide and the amine base, as these terms have been described hereinbefore, requires a critical reaction medium concentration in addition to critical random alkyl halide and amine base reactant concentrations in order to obtain the desired objective of high yields and reaction rates. The reaction medium which can be employed in the process of this invention is comprised essentially of water, methanol or mixtures of water and methanol in a weight ratio of about 10:1 to 1:10. The reaction medium has many of the properties of a solvent. However, in the process of the present invention, the reaction medium is necessary to accomplish more than simply providing a homogeneous reaction system (although in the process of this invention a homogeneous system is an advantage). The reaction medium facilitates the amination of the alkyl halide in a number of ways. A necessary property of the reaction medium is that it should be sufficiently polar to polarize the carbon/halide bond on the random alkyl halide to facilitate the halogen displacement. It is preferred that the reaction medium be capable of solvating or isolating the displaced halogen so that the amine base may attack the site from which the halogen atom has been abstracted. In addition the reaction medium should act as a solvent and be capable of dissolving both the random alkyl halide as well as the amine base used. The reaction medium concentration is a critical consideration in obtaining the unexpectedly high yields and fast reaction rates obtainable in the amination process described herein. This will be apparent on examination of the examples given hereinafter.

In the process of this invention, ammonia and amines can affect the solvent characteristics of the reaction system. Although ammonia and amines employed in the process of this invention are present in the reaction mixture primarily as reactants, they can affect the solvent characteristics of the reaction mixture. In addition the presence of the random alkyl halide may also affect the solvent properties of the reaction system. For example to aminate an extremely hydrophobic random alkyl halide (e.g., a long chain random alkyl halide) with a hydrophilic amine base (e.g., ammonia) the solvent properties of the reaction system, e.g., the solvent properties contributed primarily by the water, methanol or water/methanol mixtures as the reaction medium modified by the reactants present, can be changed to result in a more compatible reaction system. Addition of solvents or diluents such as ethanol, propanol, iso-propanol, dimethylformamide and dimethylacetamide can increase the solubility of the reactants in the reaction medium. Use of these diluents can be desirable to obtain a more efficient reactant system or to operate the process more economically. In addition to the use of the diluents listed above, mixtures of 2 or more of these diluents in varying ratios can be suitably employed where desired. Use of diluents such as ethanol, propanol, isopropanol, dimethylformamide and dimethylacetamide with water, methanol and mixtures of water and methanol as the reaction medium in a ratio of 1:10 to about 10:1 by weight is within the spirit and scope of this invention. Where such levels of diluents are used the optimum composition for a specific reaction system, e.g., random alkyl halide, amine base and reaction medium may be different from the compositions which are optimum in the absence of the diluents. Nevertheless the concentration of the reaction medium (with or without the presence of the diluents described hereinbefore) is still critical if the objects of the process of this invention are to be attained.

PROCESS CONDITIONS

The amination process of this invention can be conducted at a temperature of from about 150° F. to about 450° F. Temperatures lower than about 150° F. result in a slow reaction. Temperatures above about 450° F. promote the formation of undesired by-products. Elevated pressures are not required to accomplish the objects of this invention. However, a closed system is preferably used to minimize loss of reactants and products. Where a closed system is used elevated pressures (i.e., autogenic) are obtained. The autogenic pressures obtained will be dependent, in part, upon the reactants used, the concentrations of the reactants used, and the temperatures of operation. With volatile reactants, the pressures generated will be higher than with less volatile reactants. As has been hereinbefore stated the operating pressure during the reaction is not a critical consideration and higher pressures than those generated by the reactants can be used. Autogenic pressures are normally used. The autogenic pressures obtained will range from about 100 p.s.i.g. to about 2000 p.s.i.g. One skilled in the art can select equipment to accomplish the process of this invention without departing from the spirit and scope of this invention.

The reaction time required for the process of this invention, e.g., for the conversion of the random alkyl halide, can range from about 5 minutes to about 4 hours depending upon the particular ternary system involved. For example, for the random alkyl chlorides the time required can range from about 30 minutes to about 4 hours while for the random alkyl bromides the time required can range from about 5 minutes to about 60 minutes. With readily reactive amine bases such as methylamine and dimethylamine with the random alkyl chlorides the time required will be about 30 minutes and with the random alkyl bromides the time required will be about 5 to about 10 minutes.

REACTION PRODUCTS

The products of the reaction of the random alkyl halide and the amine base are dependent upon the specific amine base employed. For example, where the amine base is ammonia, a primary amine is obtained according to the following:

$$RX+NH_3 \rightarrow RNH_2+HX$$

Where the amine base is a primary amine such as methylamine (e.g., where R^1 is a methyl group and R^2 is hydrogen), a secondary amine is formed according to the following:

$$RX+CH_3NH_2 \rightarrow RNHCH_3+HX$$

Where the amine base is a secondary amine such as dimethylamine (e.g., where both R^1 and R^2 are methyl groups), a tertiary amine is formed according to the following:

$$RX+(CH_3)_2NH \rightarrow R\overset{\displaystyle CH_3}{\underset{\displaystyle |}{N}}CH_3+HX$$

R and X in the above three equations are as hereinbefore defined. The terms primary, secondary and tertiary, as used in the immediate preceding discussion are intended to refer to the degree of substitution of the amine bases used and the resulting amine formed rather than the positioning of the amino group on the carbon skeleton.

In the process of this reaction the hydrohalic acids formed (shown in the immediate preceding schematic equations as free hydrohalic acid) are normally tied up by neutralization with a portion of the amine base (e.g.

$$R^1\overset{\displaystyle H}{\underset{\displaystyle |}{N}}R^2 \cdot HX),$$

by neutralization of a portion of the amine formed in the reaction of the random alkyl halide and the amine base (e.g.,

$$R^1NR^2 \cdot HX)$$

or by dissolution (ionization) in the reaction system (e.g. NH_4^+ and X^-).

The reaction products can be separated from the unreacted starting materials by methods well known in the art, e.g., distillation or acid/base extraction procedures. Where it is desired the unreacted starting materials and reaction medium used can be separated from the reaction products and recycled. The process of this invention can be run as a batch or a continuous process.

In order to achieve the desired objects of this invention of increasing the reaction rate and the yields obtainable over prior art amination methods, the concentration ranges of the three components involved in the process of this invention are a critical consideration. The criticality of the reactant concentrations is illustrated in the following examples. Unless otherwise indicated weight percents are used.

EXAMPLES

General

The aminations were conducted in a 300 ml. stirred autoclave (Autoclave Engineers 300 cc. Magne Drive). An air-driven magnetic stirrer which could be varied from about 100 r.p.m. to about 1800 r.p.m. equipped with a turbine type agitator (Dispersimax) was used. The autoclave was heated externally with an electrical strip heater and internally with a steam coil (150 p.s.i.g.). Steam heat was normally used with temperatures up to about 340° F. with supplemental electrical heat being used to obtain temperatures in excess of 340° F. The autoclave temperature was controlled to within ±2° F.

The random alkyl halide and the reaction medium were charged into the autoclave and this mixture was heated to the desired reaction temperature. The amine base was charged under nitrogen pressure (from a chilled bomb) into the system once the autoclave reached the reaction temperature. Samples were withdrawn periodically through a capillary tube into sample bottles located outside the autoclave cell to follow the course of the reaction. The first 2 ml. of each of the samples was discarded because of possible contamination with sampling tube residue from the previous samplings. Once the reaction was completed, the autoclave was cooled by passing water through the steam coil. The products were discharged through a drain at the bottom of the autoclave.

The random alkyl halides used in Examples I and IV as starting materials were prepared by hydrohalogenation of α-olefins followed by randomization with a $FeCl_3$ catalyst. These random (designated *r* hereinafter) alkyl halides had no 1-isomer (e.g., terminal) present. The composition and isomer distribution of the r-alkyl halides used in these examples given hereinafter are shown in the following table:

RANDOM HALIIDE COMPOSITIION

r-Alkyl halide	r-C_{16}Cl
Halide carbon position distribution:	
2nd, percent	17.3
3rd, percent	15.3
4th, percent	11.7
5th, percent	14.9
6th–10th, percent	40.7
Purity, percent	96

Unhalogenated paraffin (20%) of equivalent chain length was added to the above r-alkyl chloride to obtain a r-alkyl chloride/paraffin mixture similar in nature to samples which can be obtained commercially. For simplicity in the examples to follow the mixture is designated hereinafter as r-C_{16} chloride or r-C_{16}Cl.

The amine bases and the reaction medium were obtained from commercial sources.

The reaction mixture at the end of the reaction period comprises internal r-alkyl amines, r-olefins (formed due to an elimination resulting in the loss of HX from the alkyl halide), unreacted r-alkyl halide, reaction medium, r-alkylamine and amine hydrohalide salts. The r-alkyl amine, r-olefin, and r-alkyl halide were removed from the reaction medium using the following extraction procedure: The reaction mixture was taken from the autoclave, warmed and stripped with nitrogen to remove any excess amine base. A 50% caustic solution, e.g., sodium or potassium hydroxide, was added to convert any r-alkyl amine salt (e.g., r-alkyl amine hydrohalide salt) to free amine to facilitate extraction of the r-alkyl amine with petroleum ether. The r-alkyl halide, r-olefin, and r-alkyl amine were then extracted with three equal portions of petroleum ether (each portion was equal to approximately twice the volume of extracted oil). The petroleum ether extract was washed once with a small quantity of water, dried with sodium sulfate and filtered. The petroleum ether was stripped off with nitrogen. Separation of the r-alkyl amine from any water insoluble materials, such as r-olefin and unreacted r-alkyl halide, was by conversion of the r-alkyl amine to the amine salt using an aqueous hydrochloric acid solution. Several extraction stages were required for a clean separation. The r-alkyl amine was recovered by making the solution basic, extracting several times with petroleum ether, back-washing once with a small amount of water, drying over sodium sulfate, filtering and driving off the petroleum ether with nitrogen.

The analytical data on the reaction products were obtained in the following manner. An F&M 720 gas chromatograph was used for rapid estimations of the reactant and product levels in the samples taken during the process. A 10 ft., ¼" diameter Carbowax column (15% diethylene glycol adipate) provided good separation of the r-olefin, r-alkyl halide and r-alkyl amine and was used to estimate percent conversion.

Elemental and functional group analysis was also used for determining final product composition. Kjeldahl nitrogen was used as an accurate method for determining percent r-alkyl amine. The percent r-alkyl halide was calculated from the halide value while the r-olefin content in the product formed as a by-product by elimination of hydrogen halide was obtained from the iodine value (IV) or hydrogen iodine value (HIV). Carbon and hydrogen values were used for checking closure to 100%. The presence of r-alkyl amine or r-olefin in a sample was easily detected by infrared spectroscopy on a Perkin-Elmer Infracord. Thin layer chromatography (TLC) was used to detect long chain or any disubstituted (i.e., dialkyl) amine formation at levels less than 1%. Dialkyl amine concentrations were also accurately measured with a high temperature (300° C.) gas chromatograph (silicone rubber column).

EXAMPLE I

Amination of r-C_{16} chloride with dimethylamine in water

The high pressure autoclave described above was washed with acetone and allowed to dry. The lines to the autoclave were cleaned by forcing acetone through them under nitrogen pressure. Water (68 g.) and alkyl chloride [80% r-C_{16} Cl and 20% paraffin C_{16}], (24 g.) were charged into the cold autoclave and sealed. A 200 ml. bomb was then chilled in a Dry Ice-acetone bath, liquid dimethylamine (108 g.) added, and the bomb was sealed. The bomb was connected to the autoclave and a high pressure nitrogen gas source.

Steam was passed through the autoclave to bring the temperature up to 265° F. and the dimethylamine was added under nitrogen pressure. The reactant mixture in the autoclave for this run was 34% water, 12% r-C_{16}

chloride and 54% dimethylamine by weight. The reaction temperature was increased to 300° F. The temperature was controlled accurately by regulating the inlet steam pressure. Vigorous stirring was continued throughout the reaction period.

At the end of ½ hr. of reaction time a 5 ml. sample was withdrawn through a capillary tube for analysis. The sample was added to 25 ml. of water made basic with sodium hydroxide. The water insolubles were extracted with three equal portions (25 ml.) of petroleum ether. The petroleum ether layer was dried with sodium sulfate and the petroleum ether stripped off with nitrogen gas. The resulting material had a light straw yellow color.

A gas chromatograph of the pertoleum ether extract indicated the composition to be 13% r-C_{16} olefin, 55% r-C_{16} dimethylamine, and 32% unreacted r-C_{16} Cl by weight. The paraffin peak on the chromatograph was observed but was ignored since it represented a nonreactive spuecies. The same sample was submitted for an iodine value, Kjeldahl nitrogen value and a chlorine value. The values obtained were corrected for the paraffin present and mole percent of r-C_{16} dimethylamine in the product mixture was calculated. The mole percentage figure so obtained was plotted as a function of the initial reaction mixture composition on a triangular graph as described below.

The above procedure was repeated with other starting compositions in which the same three compounds were used, i.e., water, dimethylamine, and r-C_{16} Cl but in which the weight proportions of the compounds were varied. The mole percentages of the desired amine product were obtained for several mixtures by running the reaction, analyzing the reaction products, and calculating the mole percentages. The results established that a critical relationship existed between the initial reactant proporions (by weight) and the rate of reaction and the yields (mole percentages) obtained. These conclusions are set forth in the triangular diagram of FIG. 1. FIG. 1 is a triangular diagram of the conventional type with each apex representing 100% of the designated component. Each of the lines parallel to the sides of the triangular diagram represent 10 weight percent. The curved graph lines A and B were drawn by joining the plotted points representing equal moral percentages of the desired amine reaction product. Thus, Line A delineates those initial reactant mixture compositions (my weight) which will yield 45 mole percent r-C_{16} dimethylamine formation after 30 minutes. Similarly, Line B represents those initial reaction mixture compositions which will yield 20 mole percent r-C_{16} dimethylamine formation.

On examination of FIG. 1, it can be seen that the formation of r-C_{16} dimethylamine is highly dependent on the initial reaction mixture proportions. For example, by changing from an initial ternary reaction mixture composition which corresponds to any point on Line B to an initial ternary reaction mixture composition which corresponds to any point on Line A it is possible to achieve an improvement of 125% in the molar percentage of the desired reaction product while still using the same reaction conditions, i.e., temperature and reaction time. An even greater increase in molar percentage of the desired reaction product can be obtained by changing the initial reaction mixture composition corresponding to a point outside of the area circumscribed by Line B to an initial reaction mixture composition corresponding to a point within the area circumscribed by Line A.

Based on the conclusions apparent from FIG. 1, the optimum initial reaction mixture composition for conversion of r-C_{16}Cl to r-C_{16} dimethylamine is an initial reaction mixture composition of about 10% r-C_{16} chloride, 60% dimethylamine and 30% water.

The results summarized in FIG. 1 demonstrate the necessity of having the initial reaction mixture compositions range within the area circumscribed by Line B. Operation of the process of this invention outside of the concentration ranges circumscribed by Line B does not result in favorable yields or reaction rates. It was unexpected with the ternary system of r-C_{16} chloride, dimethylamine, and water that the area in which favorable yields or reaction rates could be obtained would be so limited in view of the total possible initial reaction mixture compositions. In addition it was unexpected that these compositions would result in the conversion in only ½ hour since the prior art teaches that much longer reaction times are required, e.g., on the order of two to seven hours to effect conversion.

Other secondary amine bases can be substituted on an equivalent basis for the dimethylamine used in Example I above to obtain substantially similar results in that a tertiary C_{16} amine is obtained; e.g., ethylmethylamine, diethylamine, ethylpropylamine, propylmethylamine, (hydroxymethyl)methylamine, (hydroxyethyl)ethylamine, and (hydroxypropyl)methylamine.

Other random alkyl halides can be substituted on an equivalent basis for the r-C_{16} chloride used in Example I above to obtain substantially similar results in that tertiary random alkyl dimethylamines are formed; e.g.,

3-chlorononane,
6-chlorododecane,
7-chlorotetradecane,
1-chloropentadecane,
4-chlorooctadecane,
10-chloroeicosane,
2-bromooctane,
3-bromodecane,
6-bromododecane,
7-bromotetradecane,
5-bromopentadecane,
11-bromodocosane,
3-iodooctane,
5-iodoundecane,
6-iodododecane,
4-iodotridecane,
7-iodotetradecane,
2-iododhexadecane,
3-iodooctadecane,
8-iodononadecane,
4-iodotetracosane,
2-bromo-3-butyloctane,
2-bromo-3-hexyloctane,
3-chloro-5-methyldecane,
5-chloro-3-propyloctane,
2-methyl-2-chlorohexadecane, and
5-ethyl-5-bromoeicosane.

Substantially similar results are obtained where no unhalogenated paraffin is present in the r-C_{16} chloride in that r-C_{16} dimethylamine formation is obtained.

EXAMPLE II

Amination of r-C_{16} chloride with methylamine in water

The procedure described in Example I above was followed except that methylamine was substituted for the dimethylamine. The resulting ternary system composition for the run was 20% r-C_{16}Cl, 54% methylamine, and 26% water. As in Example I additional runs were made with the initial reaction mixture compositions being varied. The molar percent r-C_{16} methylamine obtained for the various initial reaction mixture compositions used permitted the construction of the triangular diagram shown in FIG. 2. FIG. 2 is a typical triangular diagram with each apex representing 100% of the designated component of the ternary system. In FIG. 2 the three components are r-C_{16} chloride, methylamine and water. Each of the lines parallel to the sides of the triangular diagram represents 10 weight percent. The Lines C and D are lines of equal r-C_{16} methylamine formation in mole percent. The Lines C and D were obtained in the same way Lines A and B were obtained in FIG. 1, i.e., by plotting the points representing the initial ternary mixtures tested and the molar

percentages of r-C_{16} methylamine obtained. The points of equal molar percentages were joined to obtain Lines C and D. Line C represents those initial ternary compositions which yield a 55 mole percent r-C_{16} methylamine formation after only 30 minutes. Line D represents those reaction mixture compositions which yield a 20 mole percent r-C_{16} methylamine formation using the same reaction conditions.

On examination of FIG. 2 it can be seen that the formation of r-C_{16} methylamine is dependent upon the initial reaction mixture concentrations. For example by making only a small change in the initial reaction mixture composition corresponding to a point on Line D to an initial reactant composition corresponding to a point on Line C results in about a 175% increase in the yield of r-C_{16} methylamine using the same reaction conditions. As even greater increase in the yields obtainable results where the initial reaction mixture composition is changed from a point falling outside of the area circumscribed by Line D into the area circumscrbed by the Line C.

Based on the conclusions summarized in FIG. 2, the optimum reaction conditions, e.g., initial compositions, is about 10% r-C_{16} chloride, 70% methylamine and 20% water.

It was unexpected that 55 mole percent r-C_{16} methylamine would be formed using a ternary reactant system of r-C_{16} chloride, methylamine, and water in only 30 minutes. The results summarized in FIG. 2 demonstrate the necessity of having the initial reaction mixture concentration within the area circumscribed by Line D. Opertion outside of this area does not result in favorable yields or reaction rates.

Other primary amines can be substituted on an equivalent basis for the methylamine used in Example II above and substantially similar results are obtained in that the corresponding r-C_{16} secondary amines are obtained; e.g., ethylamine, propylamine, (hydroxymethyl)amine, (hydroxyethyl)amine, and (hydroxypropyl)amine.

Other random alkyl halides can be substituted on an equivalent basis for the r-C_{16} chloride used in Example II above and substantially similar results are obtained in that secondary alkyl methylamines are formed; e.g.,

2-bromooctane,
3-bromodecane,
6-bromododecane,
7-bromotetradecane,
5-bromopentadecane,
11-bromodocosane,
3-chlorononane,
6-chlorododecane,
7-chlorotetradecane,
1-chloropentadecane,
4-octadecane,
10-chloroeicosane,
3-iodooctane,
5-iodoundecane,
6-iododecane,
7-iodotetradecane,
2-iodohexadecane,
3-iodooctadecane,
8-iodononadecane,
4-iododtetracosane,
2-bromo-3-butyloctane,
2-bromo-3-hexyloctane,
3-chloro-5-methyldecane,
5-chloro-3-propyloctane,
2-methyl-2-chlorohexadecane, and
5-ethyl-5-bromoeicosane.

EXAMPLE III

Amination of r-C_{16} chloride with ammonia in water

The procedure described in Example I above was followed except that ammonia was substituted for the dimethylamine and the reaction period was extended to 60 minutes. The resulting ternary system composition for the run was 20% r-C_{16}Cl, 58% ammonia and 22% water. As in Example I additional runs were made with the initial reaction mixture compositions being varied. The percent r-C_{16} amine obtained for the various initial reaction mixture compositions run permitted the construction of the triangular diagram shown in FIG. 3. In FIG. 3 the three components are r-C_{16} chloride, ammonia and water. As in FIGS. 1 and 2 Line E on the graph was drawn by joining points providing equal molar percentages of r-C_{16} amines formation. Line E represents those initial ternary reaction mixture compositions which yield 25 mole percent r-C_{16} amine formation after 60 minutes.

On examination of FIG. 3 it can be seen that the formation of r-C_{16} amine is highly dependent on the initial reaction mixture compositions. It was unexpected that with a relatively unreactive species such as the r-C_{16} chloride and ammonia, both well known in the art to be relatively unreactive species in amination processes, would result in 25 mole percent r-C_{16} amine formation in only 60 minutes of reaction time. The results summarized in FIG. 3 demonstrate the necessity of having the initial reaction mixture compositions range within the area circumscribed by Line E. Operation of the process of this invention outside of the concentration ranges circumscribed by Line E does not result in favorable yields or reaction rates.

Based on the results shown in FIG. 3, the optimum composition for the formation of r-C_{16} chloride in water using ammonia is approximately 15% water, 60% ammonia and 35% r-C_{16} chloride.

Other alkyl halides can be substituted on an equivalent basis for the r-C_{16} chloride used in Example III above and substantially similar results are obtained in that the corresponding alkyl amines are obtained; e.g., 3-chlorononane, 6-chlorododecane, 7-chlorotetradecane, 1-chloropentadecane, 4-chlorooctadecane, 10-chloroeicosane, 2-bromooctane, 3-bromodecane, 6-bromododecane, 7-bromotetradecane, 5-bromopentadecane, 11-bromodocosane, 3-iodooctane, 5-iodoundecane, 6-iododecane, 8-iodotetradecane, 2-iodohexadecane, 3-iodooctadecane, 8-iodononadecane, 4-iodotetracosane, 2-bromo-3-butyloctane, 2-bromo-3-hexyloctane, 3-chloro-5-methyldecane, 5-chloro-3-propyloctane, 2-methyl-2-chlorohexadecane, and 5-ethyl-5-bromoeicosane.

EXAMPLE IV

Amination of r-C_{16} chloride with dimethylamine in methanol

The procedure described in Example I above was followed except that methanol was substituted for the water used in Example I, the 20% added unhalogenated paraffin present in the r-C_{16}Cl used in Example I was eliminated, and the reaction period was extended to 120 minutes. The resulting ternary system composition for the run was 37% r-C_{16}Cl, 31% methanol and 32% dimethylamine. As in Example I, additional runs were made with the initial reaction mixture compositions being varied. The percent r-C_{16} dimethylamine obtained for the various initial reaction mixture compositions used permitted the construction of the triangular diagram shown in FIG. 4 in the same manner as in the preceding examples and figures. In FIG. 4 the three components at each apex of the triangular diagram are r-C_{16} chloride, dimethylamine and methanol. As in the other three figures, the Lines F, G and H were drawn by joining plotted points of equal r-C_{16} dimethylamine formation in mole percent. Line F represents those initial reaction mixture compositions which result in a 55 mole percent r-C_{16} dimethylamine formation after 120 minutes. Lines G and H represent those initial reaction mixture compositions which yield a 50 mole percent and 40 mole percent r-C_{16} dimethylamine formation, respectively, using the same reaction conditions.

On examination of FIG. 4 it can be seen that the formation of r-C_{16} dimethylamine is dependent on the initial

reaction mixture concentration. For example, by making only a small change from an initial reaction mixture composition corresponding to a point on Line H to an initial reactant composition corresponding to a point on Line F results in an increase of approximately 45% in the r-C_{16} dimethylamine formation using the same reaction conditions. An even greater increase in the yields obtained results where the initial reaction mixture composition is changed from a point falling outside of the area circumscribed by Line H into the area circumscribed by the Line F.

Based on the conclusions summarized in FIG. 4, the optimum initial reaction mixture composition to yield the greatest amount of r-C_{16} dimethylamine formation is approximately 20% r-C_{16} chloride, 40% dimethylamine, and 40% methanol.

Other secondary amine bases can be substituted on an equivalent basis for the dimethylamine used in Example IV above and substantially similar results are obtained in that a tertiary C_{16} amine is obtained; e.g., ethylmethylamine, diethylamine, (hydroxymethyl)methylamine, (hydroxyethyl)methylamine, and (hydroxypropyl)ethylamine.

Primary amines can be substituted on an equivalent basis for the dimethylamine used in Example IV above and substantially similar results are obtained in that the corresponding r-C_{16} secondary amines are obtained; e.g., ethylamine, propylamine, hydroxymethylamine, hydroxyethylamine, and hydroxypropylamine.

Ammonia can also be substituted on an equivalent basis for the dimethylamine used in Example IV above with substantially similar results being obtained in that a r-C_{16} amine is obtained.

Other random alkyl halides can be substituted on an equivalent basis for the r-C_{16} chloride used in Example IV above and substantially similar results are obtained in that the secondary alkyl dimethylamines are formed; e.g., 3-chlorononane, 6-chlorododecane, 7-chlorotetradecane, 1-chloropentadecane, 4-chlorooctadecane, 10-chloroeicosane, 2-bromooctane, 3-bromodecane, 6-bromododecane, 7-bromotetradecane, 5-bromopentadecane, 11-bromodocosane, 3-iodooctane, 5-iodoundecane, 6-iodododecane, 4-iodooctadecane, 8-iodononadecane, 4-iodotetracosane, 2-bromo-3-butyloctane, 2-bromo-3-hexyloctane, 3-chloro-5-methyldecane, 5-chloro-3-propyloctane, 2-methyl-2-chlorohexadecane, and 5-ethyl-5-bromoeicosane.

Methanol and a 1:1 methanol/water mixture can be substituted on an equivalent basis for the methanol used in Example IV above and substantially similar results are obtained in that r-C_{16} dimethylamine is obtained. In addition a 2:1 methanol/water mixture can be substituted on an equivalent basis for the methanol used in Example IV and substantially similar results are obtained in that r-C_{16} dimethylamine is obtained. In addition the methanol used in the above example can partially be replaced by diluents such as dimethylformamide, dimethylacetamide, ethanol, iso-propanol, and propanol mixtures in a ratio of 10:1 to 1:10 of the methanol to the diluents and substantially similar results are obtained.

As described herein, the present invention embodies a ternary reaction system comprised of (1) a random alkyl halide having 8 to 24 carbon atoms, (2) an amine base of the specific character described above, and (3) a reaction medium which is either water, methanol, or water/methanol mixtures. Each of these three components is essential. Each of the triangular graphs of FIGS. 1 to 4 contain curved lines which appear to come in contact with one of the sides of the triangle. Consistent with a clear understanding of the present invention, however, the curved lines do not contact the sides of the triangle for the reason that binary mixtures are not contemplated by the present invention. In FIGS. 1, 2 and 4, the curved lines are not closed by the base of the triangle (or in FIG. 2 by the right leg of the triangle for the right side of Line D). To do so would be to exclude completely the essential random alkyl halide reactant (or exclude water in the case of FIG. 2 for the right side of Line D). In this instance, at least about 1% by weight of the random alkyl halide is required in order to provide the essential three-component system of the present invention. Likewise, in FIG. 3 the curved line E is not closed by the right leg of the triangle. If it were, the triangular diagram could again be subject to misinterpretation since binary mixtures of random alkyl chloride and ammonia would appear to be contemplated. As explained above, all binary mixtures fall outside the scope of the present invention. As in FIGS. 1, 2 and 4, FIG. 3 requires at least about 1% by weight of water in order to provide the essential ternary reaction system.

As has been hereinbefore stated mixtures of water and methanol are contemplated as the reaction medium and are considered within the spirit and scope of this invention. FIGS. 1, 2, and 3 describe systems in which water is the reaction medium. FIG. 4 describes the system in which methanol is the reaction medium. More specifically FIG. 1 and FIG. 4 describe the ternary system of r-C_{16}Cl, dimethylamine and water and r-C_{16}Cl, dimethylamine and methanol respectively. Mixtures of methanol and water in a 1:10 to 10:1 ratio by weight are suitable for use as the reaction medium in the process of this invention. It will be understood that where mixtures of water and methanol are used the shape of lines circumscribing operable areas of the process of this invention will be somewhat intermediate between the shape exhibited by the lines in FIG. 1 (e.g., water alone as the reaction medium) and the shape exhibited by the lines in FIG. 4 (e.g., methanol alone as the reaction medium). It will be appreciated that where methanol and water mixtures are used as the reaction medium, the larger the proportion of water used in the methanol/water mixture, the closer the area and shape circumscribed on a triangular diagram will be to that shown in FIG. 1. Conversely the larger the proportion of methanol used in the methanol/water mixture as the reaction medium, the closer the area and shape circumscribed on a triangular diagram will be to that shown in FIG. 4.

What is claimed is:

1. A process for aminating random alkyl halides comprising the steps of:

(I) preparing a reaction mixture consisting essentially of

(A) a random alkyl halide of the formula RX wherein R is an alkyl group having from about 8 to about 24 carbon atoms and wherein X is a halogen selected from the group consisting of chlorine, bromine, and iodine, said halogen being randomly distributed on the alkyl chain;

(B) an amine base of the formula

wherein R^1 and R^2 each are selected from the group consisting of hydrogen; alkyl groups having from 1 to about 3 carbon atoms; and hydroxyalkyl groups having from 1 to about 3 carbon atoms; and

(C) a reaction medium selected from the group consisting of:

(1) water,

(2) methanol,

(3) mixtures of water and methanol, in a weight ratio of water to methanol of 1:10 to 10:1; and

(4) mixtures of (1), (2) or (3) and a diluent selected from the group consisting of:

(a) ethanol,

(b) propanol,

(c) iso-propanol,

(d) dimethylformamide, and

(e) dimethylacetamide, in a weight ratio of (1), (2), or (3) to diluent of 10:1 to 1:10;

in which the weight percents of A, B and C in said reaction mixture correspond to the following:

(1) when the amine base is one in which R^1 and R^2 each are selected from the group consisting of alkyl and hydroxyalkyl groups having from 1 to about 3 carbon atoms, and the reaction medium is water, the weight percents of A, B and C are within the area on the triangular diagram of FIG. 1 circumscribed by Line B;

(2) when the amine base is one in which R^1 is selected from the group consisting of alkyl and hydroxyalkyl groups having from 1 to about 3 carbon atoms and R^2 is hydrogen, and the reaction medium is water, the weight percents of A, B and C are within the area on the triangular diagram of FIG. 2 circumscribed by Line D;

(3) when the amine base is one in which R^1 and R^2 are both hydrogen and the reaction medium is water, the weight percents of A, B and C are within the area on the triangular diagram of FIG. 3 circumscribed by Line E;

(4) when the amine base is one in which R^1 and R_2 each are selected from the group consisting of hydrogen; alkyl groups having from 1 to about 3 carbon atoms and hydroxyalkyl groups having from 1 to about 3 carbon atoms and the reaction medium is selected from the group consisting of: methanol, mixtures of water and methanol, and mixtures of said reaction medium and a diluent selected from the group consisting of ethanol, propanol, iso-propanol, dimethylformamide, and dimethylacetamide, the weight percents of A, B and C are within the area on the triangular diagram of FIG. 4 circumscribed by Line H; and

(II) heating said reaction mixture to a temperature of from about 150° F. to about 450° F.

2. The process of claim 1 wherein R has from about 12 to about 22 carbon atoms; wherein X is chlorine; wherein R^1 and R^2 are methyl; wherein the reaction medium is water; wherein the weight percents of A, B, and C are within the area on the triangular diagram of FIG. 1 circumscribed by Line A; and wherein the temperature ranges from about 275° F. to about 400° F.

3. The process of claim 1 wherein R has from about 12 to about 22 carbon atoms; wherein X is chlorine; wherein R^1 is methyl; wherein R^2 is hydrogen; wherein the reaction medium is water; wherein the weight percents of A, B and C are within the area on the triangular diagram of FIG. 2 circumscribed by Line D; and wherein the temperature ranges from about 275° F. to about 400° F.

4. The process of claim 1 wherein R has from about 12 to about 22 carbon atoms; wherein X is chlorine, wherein R^1 and R^2 are methyl; wherein the reaction medium is methanol; wherein the weight percents of A, B and C are within the area on the triangular diagram of FIG. 4 circumscribed by Line G; and wherein the temperature ranges from about 275° F. to about 400° F.

5. The process of claim 1 wherein R has from about 12 to about 22 carbon atoms; wherein X is chlorine; wherein R^1 and R^2 are methyl; wherein the reaction medium is methanol; wherein the weight percents of A, B and C are within the area on the triangular diagram of FIG. 4 circumscribed by Line F; and wherein the temperature ranges from about 275° F. to about 400° F.

6. The process of claim 1 wherein the random alkyl halide used can contain up to about 20% unhalogenated paraffin stock.

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U.S. Cl. X.R.

252—8.8, 152; 260—584, 585; 424—325