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PREPARATION OF TETRA-ALKYL QUATERNARY AMMONIUM HALIDES

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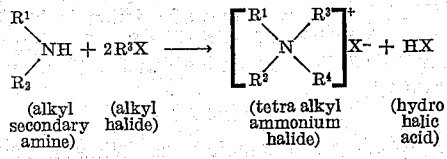
Our invention relates to the preparation of quaternary ammonium compounds, and more particularly to the preparation of tetra-alkylammonium halides by the alkylation of alkyl secondary amines with alkyl halides in the presence of sodium bicarbonate.

One well-known process of preparing quaternary ammonium compounds which is in rather widespread industrial use involves the alkylation of alkyl secondary amines with alkyl halides to produce tetra-alkyl-ammonium halides. In general, this process can be represented by the following equation:



It will be noted from the above equation that the reaction of alkyl secondary amines and alkyl halides to produce tetra-alkylammonium halides results in the production of hydrohalic acids, such as hydrochloric acid, as by-products. The presence of hydrohalic acids in the reaction mixture is undesirable in that the acids react with free amines and thereby eliminate the amines from further reaction with the alkylating agent, and thus reduce the yield of the quaternary ammonium compound from the secondary amines. A further disadvantage is that the acids tend to attack the reaction vessel if it is composed of metal, with resultant corrosion problems and discoloration of the product.

The standard practice in overcoming the problems associated with the presence of hydrohalic acids in the reaction mixture is to neutralize these acids as they are formed by strong inorganic bases such as alkali metal hydroxides. The alkaline earth metal hydroxides can also be employed with some success. For this purpose, sodium hydroxide is most frequently employed and has generally been regarded as the preferred reagent. Although the incorporation of strong inorganic bases in the reaction mixture is of value, in actual practice it is not proved to be a complete answer to the problem, or, to put it another way, the employing of strong inorganic bases has certain collateral disadvantages. Perhaps the most general of these disadvantages is that the presence of strong inorganic bases in the reaction mixture precludes the use of glass-lined equipment, and therefore metal reaction vessels must be employed. This requires the taking of extra precautions to prevent the reaction mixture from going over to the acid side and thereby corroding the metal vessel and contaminating the product. More specific problems also arise when the tendency of the alkyl secondary amine to react with the alkylating agent is relatively weak compared to the tendency of the alkylating agent to react with the strong inorganic base. This occurs when the alkyl secondary

amine is difficult to alkylate, or when the alkylating agent is particularly susceptible to hydrolysis. Under either of these conditions, the alkylating agent (alkyl halide) tends to react preferentially with the inorganic base, resulting in the hydrolysis of the alkyl halide and the formation of metallic halide salts. The disadvantages of this undesired side reaction are obvious. When it occurs to any appreciable extent, excessive amounts of both the alkylating agent and the inorganic base will be required to cause the conversion of the secondary amines to the quaternary ammonium compounds; and the product will be contaminated with metallic halide salts.

It is, therefore, an object of our invention to provide means for neutralizing the hydrohalic acid as it is formed in the reaction of alkyl secondary amines and alkyl halides and thereby avoid the disadvantages incident to allowing the hydrohalic acids to accumulate in the reaction mixture, while at the same time substantially overcoming the disadvantages associated with the use of a strong inorganic base for this purpose, such as sodium or calcium hydroxide. More specifically, it is an object of our invention to provide an improved method of preparing tetra-alkylammonium halides by the alkylating reaction described above, by means of which a higher yield and a higher purity of product can be obtained even though the secondary amine is relatively difficult to alkylate or the alkylating agent is relatively easy to hydrolyze. Further objects and advantages will appear as the specification proceeds.

A wide variety of alkyl secondary amines and alkyl halides can be used as the reagents for the production of tetra-alkylammonium halides. For example, the alkyl groups of the alkyl secondary amines can contain from 12 to 22 carbon atoms; and the alkyl group of the alkyl halide can contain from 1 to 5 carbon atoms. One important source of alkyl secondary amines is from fats and mixed oils of animal and vegetable origin such as cottonseed oil, soybean oil, corn oil, cocoanut oil, and tallow. These oils and fatty materials are composed mainly of glycerides of fatty acids in which the alkyl groups of the fatty acids contain from 12 to 22 carbon atoms, and are both saturated and unsaturated. However, during the preparation of the secondary amines by the usual methods, the unsaturated fatty acid residues are hydrogenated to the extent that the product is essentially saturated fatty acid secondary amines. Therefore, the alkyl secondary amines prepared from these raw materials are generally mixtures of secondary amines in which the alkyl groups contain from 12 to 22 carbon atoms, such as lauric, myristic, palmitic, and stearic. The most frequently occurring fatty acids contain from 12 to 18 carbon atoms, and therefore, secondary amines derived therefrom are readily available.

The availability of alkyl secondary amines in which the alkyl groups contain from 12 to 22 carbon atoms, and especially from 16 to 18 carbon atoms, has made it desirable to subject this class of secondary amines to alkylation to produce tetra-alkylammonium halides. However, the relatively long carbon chains of these amines somewhat reduce their activity compared to the shorter chain length secondary amines, and, therefore, they are relatively more difficult to alkylate. In fact, it is this class of secondary amines which was referred to above in regard to the problem of the strong inorganic base, preferentially reacting with the alkylating agent. Therefore, it is particularly desired to find a method of alkylating alkyl secondary amines in which the alkyl groups contain from 12 to 22 carbon atoms by means of which high yields can be obtained and the formation of metallic halide salts can be avoided.

While, as indicated above, alkyl halides can be employed in which the alkyl groups contain from 1 to 5

carbon atoms, it is generally preferred to use either methyl or ethyl halides as alkylating agents, and particularly methyl halides, since they can be introduced into the reaction mixture as a gas. While all of the methyl and ethyl halides are operative, it is preferred to employ either the chlorides or bromides. It has been found that the alkyl bromides are more susceptible to hydrolysis by the action of a strong inorganic base than the alkyl chlorides, although both exhibit this tendency to a disadvantageous degree when used in alkylating alkyl secondary amines having relatively long chain alkyl groups. Therefore, when employing, for example, methyl bromide, as an alkylating agent, unsatisfactory results are generally obtained when sodium hydroxide or calcium hydroxide is used to neutralize the hydrobromic acid formed in the reaction mixture.

We have now discovered that by employing sodium bicarbonate instead of sodium hydroxide or calcium hydroxide, to neutralize the hydrohalic acid as it is formed, improved results are obtained in that the reaction time for the complete conversion of the secondary amine to the quaternary compound can be materially shortened, and that the specific problems discussed above are substantially overcome. More specifically, we have discovered that the presence of sodium bicarbonate in the reaction mixture in a sufficient amount to neutralize the hydrohalic acid as it is formed allows alkyl secondary amines in which the alkyl groups contain from 12 to 22 carbon atoms to be alkylated in a shorter reaction time and with a higher yield than has heretofore been possible. Also, we have found that the use of sodium bicarbonate instead of a strong inorganic base in the reaction mixture permits the use of alkyl bromides such as methyl bromide as alkylating agents, while obtaining excellent results in terms of yield and purity of product.

In general, our modified reaction can be carried out in the same way as the previous processes of reacting alkyl secondary amines with alkyl halides to produce tetra ammonium halides, except that an amount of sodium bicarbonate is added to the reaction mixture equivalent to the amount of sodium hydroxide or calcium hydroxide which was previously employed. For example, the alkyl secondary amine, water, and sodium bicarbonate can be charged into a pressure reaction vessel into which the methyl chloride or bromide can be introduced under elevated pressure, the reactants being maintained at from 90 to 100° C. With this procedure, the reaction can be expected to be completed in from 4 to 8 hours. It will be understood that the process details such as reaction temperatures and pressures can be varied considerably according to well-known practices, and other solvents such as the lower alcohols, can be employed instead of water. If the reaction proceeded stoichiometrically, it would be expected that about one mole of neutralizing agent would be required for each mole of secondary amine to neutralize the hydrohalic acid as it is formed. However, as indicated above, when strong inorganic bases are employed as the neutralizing agents, such as sodium and calcium hydroxides, it is frequently necessary to add a considerable excess of the neutralizing agent over an equal molar quantity, to complete the reaction, since a portion of the neutralizing agent is lost by reacting with the alkylating agent. When employing sodium bicarbonate, however, there is relatively little tendency for the neutralizing agent to react with the alkylating agent, and, therefore, an equimolar quantity of sodium bicarbonate is generally sufficient. However, there is no particular disadvantage to using an excess of sodium bicarbonate, except that the reactant is wasted. In addition, glass-lined equipment can be employed and, therefore, it is not necessary to prevent the reaction mixture from going over to the acid side at or near completion of the reaction, which permits of the required amount of sodium bicarbonate without a large excess, although a slight excess may sometimes be desirable.

In order that our process can be better understood, and particularly so that its advantages can be compared with prior-art processes, we wish to set out the following illustrative examples:

Example I

1,000 parts by weight of tallow secondary amines (having alkyl groups composed mainly (90%) of palmityl and stearyl fatty acid residues; the oleyl and linolyl residues having been substantially converted to stearyl residues), 80 parts by weight of anhydrous sodium hydroxide, and 700 parts by weight of water, were charged to a stainless steel one-gallon autoclave equipped with an agitator. The approximate molecular weight of the di-tallow secondary amine was 560. The reactor was closed and methyl chloride was introduced into the unit at 75 pounds p. s. i. g. and the reaction mixture was stirred and heated to 100° C. for eight hours, the secondary amine was only 69% converted and the mixture no longer contained any free sodium hydroxide. Therefore, an additional 40 parts of sodium hydroxide was added, and the reaction was continued under the previous conditions. After eight hours at temperature, the secondary amine was found to be 85% converted.

Example II

This run was carried out according to the procedure of Example I for 8 hours with the following charge: 1,000 parts by weight of tallow secondary amine (app. mol. wt. 560), 77 parts by weight of calcium hydroxide, and 700 parts by weight of water. After 8 hours at temperature (100° C.), the amine was 83.1% converted to quaternary.

Example III

The procedure of Example I was followed, except that the temperature was maintained at 90° C. for 8 hours with the following charge: 1,000 parts by weight of coco secondary amine (app. mol. wt. 410 having its alkyl groups composed mainly of lauryl and myristyl radicals), 95 parts by weight calcium hydroxide, and 700 parts by weight of water. The product indicated 77% conversion to quaternary.

Example IV

The procedure of the preceding examples was followed with the temperature being maintained at 100° C. and a reaction time of 8 hours with the following charge: 1,000 parts by weight of tallow secondary amine (app. mol. wt. 560), 75 parts by weight calcium hydroxide, 250 parts by weight n-butanol, and 400 parts by weight of water. The product analyzed to show 87.3% conversion to quaternary.

Example V

This run was made according to the same procedure at 100° C. for 8 hours with the following charge: 1,000 parts by weight coco secondary amine (app. mol. wt. 410, having its alkyl groups composed mainly (80%) of C 12 and C 14 fatty acid residues, namely, lauryl and myristyl), 95 parts by weight calcium hydroxide, and 700 parts by weight of water. The product analyzed to show 77% conversion to quaternary.

Example VI

Following the same procedure, a run was made at 100° C. for 8 hours with the following charge: 1,000 parts by weight coco secondary amine (app. mol. wt. 430), 95 parts by weight calcium hydroxide, and 700 parts by weight water. The product analyzed to show 80% conversion to quarternary.

Example VII

This run was made at 100° C. for 8 hours with the following charge: 1,000 parts by weight tallow second-

ary amine (app. mol. wt. 560), 500 parts n-butanol, and 85 parts calcium hydroxide. The product analyzed to show 74.5% conversion to quaternary.

Example VIII

Run VIII was run as previously, except that the temperature was maintained at 7° C. for 8 hours and methyl bromide was used as the alkylating agent with the following charge: 1,000 parts by weight coco secondary amine (app. mol. wt. 430), 95 parts by weight calcium hydroxide, and 500 parts by weight water. The product analyzed to be only 62% converted. An additional 50 grams of calcium hydroxide were added and the heating continued. The final product then analyzed as being 70% converted to quaternary.

Example IX

The procedure of the preceding examples was followed with the temperature maintained at 100° C. for 5 hours and with methyl bromide as the alkylating agent for the following charge: 1,000 parts by weight coco secondary amine (app. mol. wt. 435), 200 parts by weight sodium bicarbonate, and 500 parts by weight water. The reaction was vented once an hour. The product analyzed as being 89% converted to quaternary.

Example X

Following the same procedure, a run was made for 6 hours using methyl bromide as the alkylating agent with the following charge: 1,000 parts by weight coco secondary amine (app. mol. wt. 407), 240 parts by weight sodium bicarbonate, and 500 parts by weight water. The product analyzed as being over 95% converted to quaternary.

Example XI

This run was made at 100° C. for 6 hours with methyl chloride as the alkylating agent for the following charge: 1,000 parts by weight tallow secondary amine (app. mol. wt. 560), 175 parts by weight sodium bicarbonate, and 750 parts by weight water. This product analyzed as being over 95% converted to quaternary.

Example XII

Following the same procedure, a run was made at 100° C. for 6 hours using methyl chloride as the alkylating agent for the following charge: 1,000 parts by weight coco secondary amine (app. mol. wt. 423), 230 parts sodium bicarbonate, and 750 parts water. The product analyzed as being over 95% converted to quaternary.

Example XIII

This run was made at 100° C. for 8 hours with methyl chloride as the alkylating agent for the following charge: 1,000 parts by weight tallow secondary amine (app. mol. wt. 560), 175 parts by weight sodium bicarbonate, and 750 parts by weight water. The product analyzed to show 95% conversion to quaternary.

A summary of the results of the runs set out in the foregoing examples is presented in the following table:

Run No.	Alkyl Secondary Amine	Alkyl Halide	Inorganic Base	Time, Hours	Percent Conversion
1	Tallow	CH_3Cl	NaOH	8	69
1a	do	CH_3Cl	(more added)	16	85
2	do	CH_3Cl	$Ca(OH)_2$	8	83.1
3	do	CH_3Cl	$Ca(OH)_2$	8	77
4	do	CH_3Cl	$Ca(OH)_2$	8	87.3
5	Coco	CH_3Cl	$Ca(OH)_2$	8	77.0
6	do	CH_3Cl	$Ca(OH)_2$	8	80.0
7	Tallow	CH_3Cl	$Ca(OH)_2$	8	74.5
8	Coco	CH_3Br	$Ca(OH)_2$	8	62.0
9	do	CH_3Br	$NaHCO_3$	5	89.0
10	do	CH_3Br	$NaHCO_3$	6	95.0
11	Tallow	CH_3Cl	$NaHCO_3$	6	95.0
12	Coco	CH_3Cl	$NaHCO_3$	6	95.0
13	Tallow	CH_3Cl	$NaHCO_3$	6	95.0

It will be apparent from the foregoing that sodium bicarbonate can advantageously be employed in the process of preparing quaternary ammonium compounds by reacting secondary amines with alkyl halides. While the use of sodium bicarbonate instead of a strong inorganic base is particularly advantageous when the secondary amine reactant contains two long chain alkyl groups, it is also useful with other secondary amine reactants. In fact, secondary amines containing either two aryl groups or an aryl group and an alkyl group present similar problems to the long chain alkyl secondary amines. It will be understood that such secondary amines are included within the scope of this invention.

While in the foregoing specification, we have set forth specific details of our process for the purpose of illustration, it will be apparent to those skilled in the art that many of these details can be varied widely without departing from the spirit of our invention.

We claim:

1. In a process of preparing a quaternary ammonium compound, the step comprising reacting one mole of an alkyl secondary amine in which the alkyl groups contain from 12 to 22 carbon atoms with more than one mole of an alkyl halide in which the alkyl group contains from 1 to 5 carbon atoms, in the presence of a sufficient amount of sodium bicarbonate to neutralize the hydrohalic acid produced by the reaction as it is formed and to maintain the reactants at a basic pH without promoting hydrolysis of the alkyl halide.

2. In a process of preparing a quaternary ammonium compound, the step comprising reacting one mole of an alkyl secondary amine in which the alkyl groups contain from 12 to 18 carbon atoms with more than one mole of alkyl halide in which the alkyl group contains from 1 to 5 carbon atoms, in the presence of a suffiicient amount of sodium bicarbonate to neutralize the hydrohalic acid produced by the reaction as it is formed and to maintain the reactants at a basic pH without promoting hydrolysis of the alkyl halide.

3. In the process of preparing a tetraalkylammonium halide, the step of reacting one mole of an alkyl secondary amine in which the alkyl groups contain from 12 to 22 carbon atoms with approximately two moles of an alkyl halide containing from 1 to 5 carbon atoms selected from the group consisting of alkyl chlorides and alkyl bromides in the presence of at least about 1 mole of sodium bicarbonate for each mole of said alkyl secondary amine to neutralize the hydrohalic acid as it is formed and to maintain the reactants at a basic pH without promoting hydrolysis of the alkyl halide.

4. In a process of preparing a tetraalkyl ammonium bromide, the step of reacting one mole of an alkyl secondary amine with more than one mole of an alkyl bromide containing from 1 to 5 carbon atoms in the presence of at least about 1 mole of sodium bicarbonate per mole of said amine to neutralize the hydrobromic acid as it is formed and to maintain the reactants at a basic pH without promoting hydrolysis of the alkyl halide.

5. In a process of preparing a tetraalkylammonium halide, the step of reacting one mole of an alkyl secondary amine in which the alkyl groups contain from 12 to 22 carbon atoms with approximately two moles of an alkyl halide selected from the group consisting of methyl chloride and methyl bromide in the presence of sufficient sodium bicarbonate to neutralize the hydrohalic acid as it is formed in the reaction mixture and to maintain the reactants at a basic pH without promoting hydrolysis of the alkyl halide.

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