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PREPARATION OF N-ALIPHATIC MORPHOLINES

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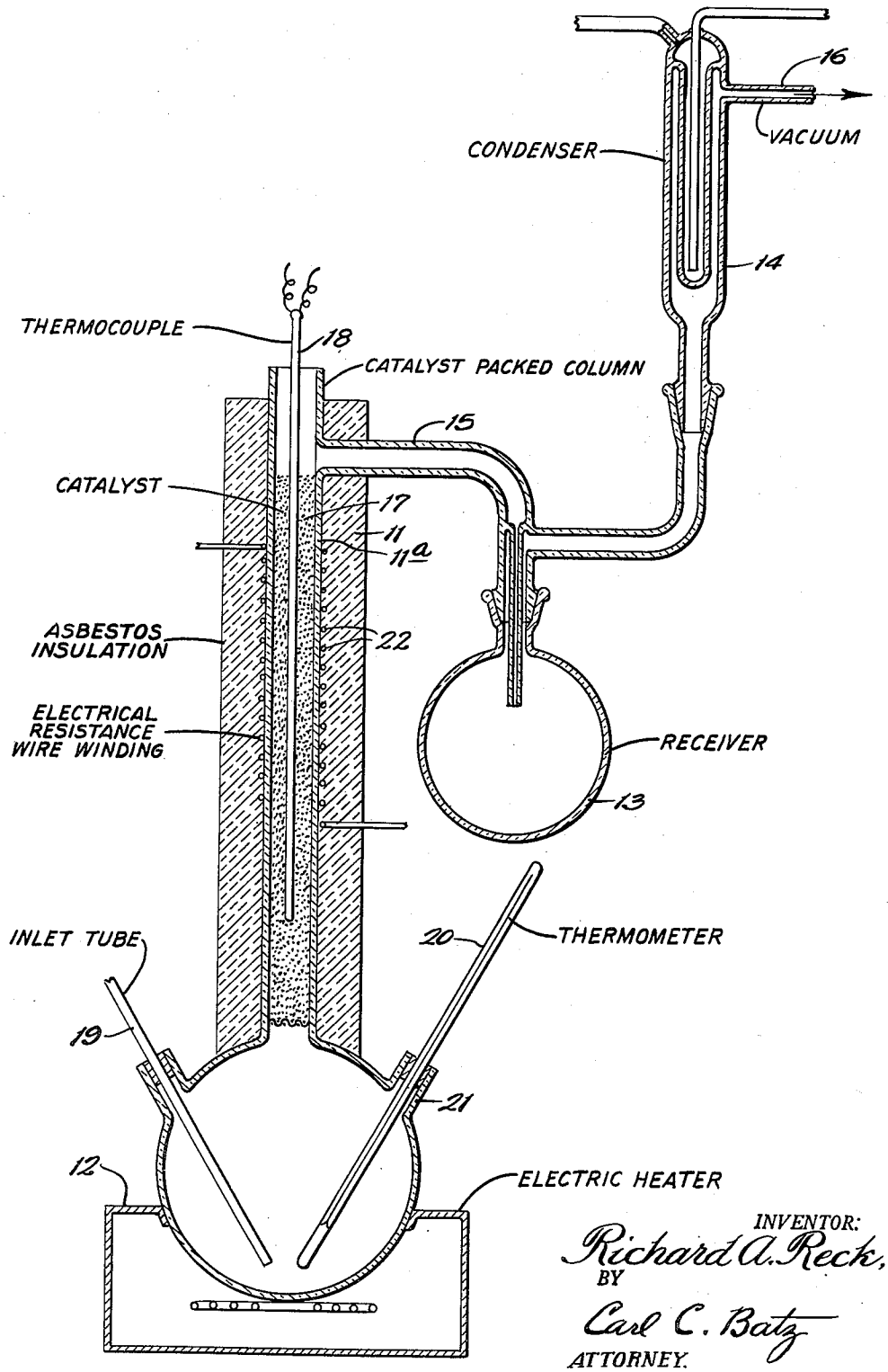

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PREPARATION OF N-ALIPHATIC MORPHOLINES

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9 Claims. (Cl. 260—247)

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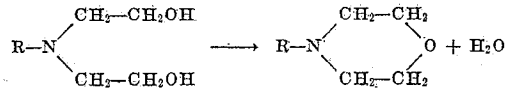
This invention relates to the preparation of N-aliphatic morpholines. More particularly, the invention is concerned with the preparation of these compounds from bis (2-hydroxyethyl) aliphatic amines by vapor phase treatment. This is a continuation-in-part of my co-pending application U. S. Ser. No. 105,548, filed July 19, 1949, now abandoned.

N-aliphatic morpholines are needed for large scale production in the preparation of other chemicals. One well established class of compounds, whose members are easily made from N-aliphatic morpholines, are the quaternary ammonium salts. These substances have well-known uses as wetting agents, textile assistants, bactericides and surface active agents. However, heretofore N-aliphatic morpholines have not been available in large volume because of the difficulty of preparing these compounds.

It is an object, therefore, of the present invention to provide a simple and inexpensive method for the preparation of N-aliphatic morpholines in large volume. A further object is to provide a method for the production of aliphatic morpholines in a simple, efficient and continuous manner for making them available in quantity for the production of quaternary ammonium salts, and other products. Yet another object is to provide a process by which N-aliphatic morpholines may be produced quickly and in volume through the vapor phase dehydration of bis (2-hydroxyethyl) alkyl amines. Other specific objects and advantages will appear as the specification proceeds.

The process can be represented in general by the equation:



wherein R is an aliphatic radical such as an alkyl or an alkylene radical. This cyclization of bis (2-hydroxyethyl) aliphatic amines is carried out in the vapor phase in the presence of a dehydration catalyst, and preferably at a temperature of between 300 to 400° C.

The process may be carried out in various types of apparatus and, for the purpose of illustration, there is set out in the accompanying drawing a schematic view of apparatus in which one embodiment of my process may be employed.

In the illustration given in the drawing, there is a three-necked flask 10, a column 11 providing a catalyst chamber 11a, an external heating element 12, a receiver or receiving flask 13, and a condenser 14. The column providing the catalyst

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chamber is attached to the center neck of the three-necked flask 10, which may be called a "reservoir flask." The vertical catalyst column is provided near its top with a tube 15 leading to the receiving flask 13. To the receiving flask 13 there is attached a condenser 14 which, in turn, is equipped with an outlet pipe 16 leading to a source of suction, so that, when desired, the whole system may be maintained at reduced pressure.

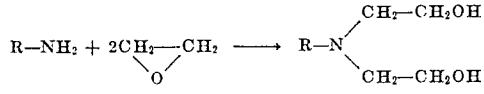
In the catalyst chamber 11a is placed a dehydrating catalyst material 17. A thermocouple 18 may be extended through the body of the catalyst and may have lead lines connected to a suitable indicator instrument. In the operation of the process, a bis (2-hydroxyethyl) aliphatic amine is continuously admitted to the reservoir flask 10 through the inlet pipe 19. The temperature in the interior of the flask may be indicated by a thermometer 20, which extends through the neck 21 of the flask 10. Heat is then applied to the bottom of the reservoir flask to bring the temperature sufficiently high to vaporize the bis (2-hydroxyethyl) aliphatic amines therein. As the vapors of the material pass upwardly, they come into contact with the catalyst in the catalyst chamber. The temperature of the catalyst is kept somewhat above the vaporization point of the aliphatic amines by means of an external heating coil 22, which may be formed of electric resistance wire, etc. As the aliphatic amines pass through the catalyst chamber they are dehydrated and immediately internally condensed to form the N-aliphatic morpholines. Said morpholines then pass to the receiving flask where they are condensed and collected.

When preparing N-aliphatic morpholines having a long chain aliphatic group attached, I find it best to carry out the reaction under vacuum. By this means, decomposition of the bis (2-hydroxyethyl) aliphatic amines is prevented, since the temperature necessary to vaporize them in vacuum is considerably lower than at atmospheric pressure. Usually a vacuum of 30 mm. will suffice for aliphatic amines containing up to 22 carbon atoms. In preparing N-aliphatic morpholines having a short chain length, the reaction may be conveniently carried on under atmospheric pressure. Specifically I prefer, however, to carry on the process at about atmospheric pressure when the aliphatic amines contain from about 1 to 5 carbon atoms, and under vacuum when the aliphatic amines contain from about 6 to 22 carbon atoms.

The temperature may be varied within substantial limits in the practice of the process. In

the reservoir flask, the temperature is ordinarily lower than the temperature in the catalyst chamber. This is because the temperature in the reservoir flask need only be high enough to vaporize the aliphatic amine, while the catalyst chamber temperature must be high enough to dehydrate and bring about the reaction described. The latter temperature might be called "the reaction temperature" and, under the conditions set out, I found the temperature range to be critical. This range should be from 300° C. to 400° C. Excellent results have been obtained with a variety of aliphatic amines at temperatures of from 320° to 360° C.

Bis (2-hydroxyethyl) aliphatic amines may be produced by any of the various known methods. For example, they may be produced with comparative ease by reacting the aliphatic amine with ethylene oxide, as represented by the following equation:



wherein R is an aliphatic radical such as an alkyl or alkylene radical.

The aliphatic or R group attached to the nitrogen in the bis (2-hydroxyethyl) aliphatic amine may contain 1 to 22 carbon atoms in a straight or branched chain and may be saturated or unsaturated. Examples of such radicals when the aliphatic group is saturated are methyl, ethyl, propyl, butyl, isobutyl, amyl, isoamyl, valeryl, caproyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, myristyl, palmityl, stearyl, etc. When the aliphatic group is unsaturated, the R group may be: vinyl, propylene, butylene, isobutylene, amylene, isoamylene, octylene, decylene, linoleyl, oleyl, sorbyl, linolinyl, etc.

Any dehydration catalyst may be employed. Aluminum oxide, chromium oxide, iron oxide, potassium acid sulphate, pumice, and other well-known dehydrating catalysts, are useful in the dehydration step described.

Specific examples of the process may be set out as follows:

EXAMPLE I

N-dodecyl morpholine

In the apparatus previously described was placed 100 g. of bis (2-hydroxyethyl) dodecyl amine. The pot was heated by means of a cone heater to 275° C. The temperature of the catalyst tube (Al_2O_3) was 340° C. Vacuum was applied (30 mm.) and at 275° C. the amine began to vaporize and the N-dodecyl morpholine started to collect in the receiving flask along with water. After 30 cc. was collected, the pot temperature was raised to 290° C. and held there for the remainder of the run (2 hours). Total distillate 80 g. plus a few grams of water, which was discarded. The product was distilled almost quantitatively at 130°–135° C./1 mm. yield 82%. The crude N-dodecyl morpholine was fractionally distilled through a Stedman column and a middle cut showed a molecular weight of 260 by titration with HCl. Theory for N-dodecyl morpholine 255.

EXAMPLE II

N-soya morpholine

Commercial quality bis (2-hydroxyethyl) soya amine, consisting mainly of bis (2-hydroxyethyl) oleyl amine and bis (2-hydroxyethyl) linoleyl amine, was treated in a similar manner. In this case, 300 cc. of bis (2-hydroxyethyl) soya amine

was placed in an addition funnel attached to one of the necks of the flask. Vacuum was applied to the system (20 mm.) and the catalyst tube, packed with aluminum oxide pellets, was heated to 330° C. The temperature of the reaction pot was raised until vaporization of the starting material began at 300° C. The temperature in the pot was maintained at 300°–330° C. for the remainder of the run. After about 50 cc. of product was collected, the bis (2-hydroxyethyl) soya amine from the addition funnel was added to the reaction pot at a rate about equal to the vaporization. In all, 270 cc. of product was collected along with 20 g. of water. The water was separated and the N-soya morpholine distilled at 180°–205° C./0.5 mm., yield 250 cc., 79%.

EXAMPLE III

Heptyl morpholine

In this example, the vaporization point is somewhat lower than in the previous cases. The reaction pot is charged with 34 g. bis (2-hydroxyethyl) heptyl amine. The catalyst tube, packed with aluminum oxide pellets, is heated to 300° C. and the pot heated to 250° C. The vacuum is applied and gradually increased until the amine vaporizes. This occurs when the height of a column of mercury reaches 45 cm. The pressure is maintained at this point for the remainder of the run, with the pot temperature at 250°–280° C. and the column at 300°–360° C. 28 g. of N-heptyl morpholine was obtained. B. P. 92° C./14 mm.

EXAMPLE IV

Quaternary preparation

Quaternary ammonium salts of the above prepared N-soya morpholine and N-dodecyl morpholine were made by heating the amines with excess methyl chloride at 120° C. for 2 hours. The quaternary ammonium chlorides showed excellent water solubility and have definite germicidal, bactericidal and surface active agent characteristics.

EXAMPLE V

Ethyl morpholine

In this case, no vacuum need be applied because of the relatively low boiling point of bis (2-hydroxyethyl) ethyl amine. However, to retard darkening of the product, a slow stream of nitrogen gas was bubbled through the reaction. 67.5 g. (0.5 mole) of bis (2-hydroxyethyl) ethyl amine was placed in the reaction flask. Heating of the flask and column was started; column heated to 330°–340° C. and the pot to 255°–260° C. At these temperatures, ethyl morpholine began to appear in the receiver, and at the end of 2 hours 50 g. of crude product was collected. Distillation yielded 35 g. of ethyl morpholine; B. P. 138°–145° C.

EXAMPLE VI

N-undecylenicmorpholine

In the apparatus previously described was placed 35 g. of bis(2-hydroxyethyl)-undecylenic-amine. The pot was heated to 250° C. and the catalyst chamber was heated to 345° C. Vacuum was applied (32 mm.) and the N-undecylenic-morpholine began to appear in the receiver along with a small quantity of water. The reaction was allowed to proceed until no more liquid was collected (2 hours). A total of 22 g. of distillate was collected. The N-undecylenicmorpholine was separated from the lower water layer and was

dried over potassium carbonate. Distillation gave 19 grams of product boiling at 165–170° C./10 mm. Yield 58%.

EXAMPLE VII

N-octadecenylmorpholine

Bis(2 - hydroxyethyl) octadecenylamine (34 grams) was added to the vaporizer of the apparatus previously described. Vacuum was applied to the system and the heating was regulated at 300° C. in the pot and 330° C. in the catalyst tube. At these temperatures there was a slow distillation of N-octadecenylmorpholine into the receiver. Drying and distillation gave 26 g. of N - octadecenylmorpholine boiling at 190–195° C./0.5 mm. Yield 79%.

While in the foregoing specification, I have set out specific operating conditions and reactants of any process to better illustrate embodiments of my invention, it will be understood that such details can be varied widely by those skilled in the art without departing from the spirit of my invention.

I claim:

1. The process of preparing N-aliphatic morpholines, which comprises cyclizing bis (2-hydroxyethyl) aliphatic hydrocarbon amines in the vapor phase at from 300–400° C. while in contact with a dehydration catalyst.

2. The process for preparing N-aliphatic morpholines, which comprises producing a ring closure in a molecule of a bis (2-hydroxyethyl aliphatic hydrocarbon amine selected from the group consisting of bis (2-hydroxyethyl) alkyl amines and bis (2-hydroxyethyl) alkylene amines by contacting said aliphatic amine molecule in vapor form at from 300–400° C. with a dehydration catalyst to eliminate water from said molecule and thereby effect said ring closure.

3. The process of preparing N-alkyl morpholines, which comprises cyclizing bis (2-hydroxyethyl) alkyl amines in the vapor phase at from 300–400° C. while in contact with a dehydration catalyst.

4. The process of preparing N-alkylene morpholines, which comprises cyclizing bis (2-hydroxyethyl) alkylene amines in the vapor phase at from 300–400° C. while in contact with a dehydration catalyst.

5. In a process for preparing N-aliphatic morpholines, the steps of vaporizing bis (2-hydroxyethyl) aliphatic hydrocarbon amines, and passing the vapors thereof at a temperature in the range of about 300°–400° C. in contact with a dehydration catalyst.

6. In a process for preparing N-aliphatic morpholines, the steps of vaporizing bis (2-hydroxyethyl) aliphatic hydrocarbon amines, passing the vapors thereof at a temperature in the range of about 300°–400° C. in contact with a dehydration catalyst, and condensing the vapors.

7. In a process for preparing N-aliphatic morpholines, the steps of vaporizing bis (2-hydroxyethyl) aliphatic hydrocarbon amines, passing the vapors thereof at a temperature in the range of about 320°–360° C. in contact with a dehydration catalyst, and condensing the vapors.

8. In a continuous process for preparing N-aliphatic morpholines, the steps of continuously passing vapors of a bis (2-hydroxyethyl) aliphatic hydrocarbon amine at a temperature of about 300°–400° C. through a dehydration zone and in contact with a dehydration catalyst, and continuously withdrawing and condensing the vapors from said zone.

9. In a continuous process for preparing N-aliphatic morpholines, the steps of continuously vaporizing a bis (2-hydroxyethyl) aliphatic hydrocarbon amine, passing the vapors at a temperature of about 300°–400° C. through a dehydration zone maintained under vacuum, and in contact with a dehydration catalyst, and continuously withdrawing and condensing the vapors from said zone.

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