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PROCESS FOR PRODUCING LACTAMS

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This invention relates to a process for the rearrangement of cyclic ketoximes to lactams, and still more particularly to a process for the rearrangement of cyclohexanone oxime to ε-caprolactam by means of sulfuric acid.

It is known to the art that cyclic ketoximes rearrange to lactams, but prior investigators, in carrying out this rearrangement, soon realized that due to the violently exothermic character of the reaction, certain precautions must be taken in order to minimize danger of serious explosions. For this reason they found it necessary to dissolve the ketoxime in sulfuric acid or in a mixture of sulfuric and acetic acids and to heat that solution under very carefully controlled conditions or else to dissolve the ketoxime in part of the sulfuric acid and to add that solution under carefully controlled temperature conditions to the remainder of the acid. It therefore had become an accepted fact that ketoximes could not be rearranged in an acid solution except when properly diluted. These prior processes are not susceptible of successful adaptation to large scale operation because the heating of large amounts of solution of ketoxime in acid involves the danger of the reaction running away and because of added expense due to the multiplicity of steps necessary for carrying out these reactions.

It is therefore the object of this invention to provide a method for carrying out the rearrangement of cyclic ketoximes to lactams which shall be safely adaptable to large scale operations. Another object is the production of caprolactam by the rearrangement of cyclohexanone oxime. Other objects will be apparent from the reading of the following description of the invention.

These objects are accomplished by the following process which comprises maintaining sulfuric acid above the threshold temperature for the rearrangement reaction preferably between the temperature of 90 and 130° C. while adding the cyclic ketoxime thereto. More specifically this process comprises heating a sulfuric acid of a concentration in excess of 75% to a temperature between 90 and 130° C., removing the source of heat and then adding the cyclic ketoxime in portions and at such a rate that the temperature is maintained by the heat of reaction. By carrying out the reaction in the manner described the rearrangement takes place smoothly without the explosive violence generally characteristic. During the adding of the cyclic ketoxime, the sulfuric acid mixture may be subjected to cooling so as to remove any excess amount of heat of reaction that would tend to bring the reaction mixture above a temperature of 130° C. The resulting lactams may be recovered by pouring the sulfuric acid solution on ice and neutralizing it.

A complete and detailed description of this process is contained in the following examples, which illustrate but do not limit the invention.

Example I

A 500 cc. 3-necked flask was equipped with a thermometer and stirrer and charged with 180 cc. of 90% sulfuric acid. The acid was stirred and heated to 90–95° C. The source of heat was then removed and 90 grams of cyclohexanone oxime was added in small portions at such a rate that the temperature of the reaction mixture remained at 90–95° C. When all of the oxime had been added the solution was heated and stirred at 95° for 40 minutes. It was then cooled to 10° C. and slowly poured into 360 grams of chipped ice. The solution was set in an ice bath and immediately neutralized with 50% sodium hydroxide, keeping the temperature below 60° C. The resulting oil was then separated from the aqueous layer and the latter was extracted with three 100-cc. portions of chloroform. The chloroform extracts were combined, the solvent distilled and the residue combined with the oil originally separated. This oil was then distilled under reduced pressure, discarding a small forerun of unchanged oxime and collecting the fraction boiling from 118–127° C. at 4–6 mm., which solidified in the receiver. The distilled product weighed 78.5 grams (87% of theoretical).

Example II

One hundred cc. of 90% sulfuric acid was heated to 90–95° C. and then maintained at that temperature by the gradual addition of 48 grams of cyclopentanone oxime. The solution was then held at 95° C. for one-half hour following addition of the oxime, then cooled to 10° C., poured into 200 grams of chipped ice and then neutralized with 50% sodium hydroxide. The resulting solution was extracted with three 150-cc. portions of chloroform; the chloroform was then evaporated on a steam bath and the residual oil distilled under diminished pressure. Twenty-five and a half grams of δ-valerolactam, boiling at 127–130°/11 mm., was collected; this corresponds to a yield of 53%.

Example III

One hundred cc. of 90% sulfuric acid was heat-

ed to 90–95° C. and cyclohexanone oxime was added at a rate sufficient to maintain the temperature at this point until the addition of oxime no longer produced an exothermic reaction. This required 176.5 g. of oxime, and the final mole ratio of acid to oxime was 1.26:1. The mixture was heated at 95° C. for a half hour, cooled, poured on 200 g. of ice, and neutralized with 50% sodium hydroxide. The oily layer was separated and the aqueous layer was extracted with three 100-cc. portions of chloroform. The chloroform extracts were then combined with the oily layer first separated, the chloroform distilled on a steam bath, and the residual oil distilled under diminished pressure. There was obtained 113 g. of crude caprolactam.

Example IV

Five thousand six hundred seventy-five cc. of 90% sulfuric acid was heated to 90–95° C. and 3 kg. of cyclohexanone oxime (ratio of acid to oxime 3.5 moles to 1) was added at such a rate that the temperature of the reaction mixture remained at 90–95° C. (1¼ hours was required for this addition). The mixture was heated 1 hour at 95° C., then cooled, poured into 7,500 g. of chipped ice, and neutralized with 12 l. of concentrated aqueous ammonia, keeping the temperature below 40° C. The oily layer was separated and the aqueous layer extracted with 4,500 cc. of chloroform. The chloroform solution was then added to the oily layer, separated from a small amount of water, and then washed with a saturated sodium chloride solution containing 10% sodium hydroxide. The chloroform solution was finally treated with solid calcium chloride, filtered, and distilled. There was obtained 1,966 g. (65%) of ε-caprolactam.

The mole ratio of sulfuric acid to oxime is a function of the nature of the oxime and of the concentration of acid. Using 90% sulfuric acid and cyclohexanone oxime, continued addition of oxime produced an exothermic reaction until a point was reached at which the mole ratio of acid to oxime was 1.3:1; this appears to be the lower limit of the ratio of acid to oxime. For cyclohexanone oxime and 90% sulfuric acid, use of a sufficient quantity of the latter to give a final mole ratio of 3.5:1 gives a clean cut reaction and very good yields.

The strength of sulfuric acid to be used may be varied within wide limits, according to the ease with which the rearrangement occurs. Generally sulfuric acid varying from about 75% to about 90% may be used with good results. The particular concentration of acid used in any one case depends upon the oxime being treated, thus, for example, commercial concentrated acid (96%) gives good results with cyclohexanone oxime; for oximes easier to rearrange the more dilute acids may be used.

In the practice of this invention temperatures varying from about 90° to 130° C. may be used in the rearrangement reaction. Generally, it is preferred to operate at temperatures from about 90° to about 100° C. The particular temperature, however, depends to a certain extent upon the oxime being treated, thus, for example, for the rearrangement of cyclohexanone oxime a temperature range of 90–95° has been found to give a smooth, controllable reaction and good yields. For more sensitive oximes better yields will result from the use of a lower temperature (and less concentrated acid). On the other hand, oximes less readily rearranged will require a higher range of temperature to insure a smooth, continuous reaction.

The invention is generally applicable to cyclic ketoximes, as, for example, cyclohexanone oxime, cycloheptanone oxime, cyclooctanone oxime, cyclopentadecanone oxime, cyclohexadecanone oxime, cyclopentanone oxime, 2-methylcyclopentanone oxime, 2 methylcyclohexanone oxime, 4-tertiary butylcyclohexanone oxime, β-tetralone oxime, menthone oxime, and other unsubstituted and substituted cyclic ketoximes.

The method of isolating the product depends on the characteristics of the lactam. Bases other than sodium hydroxide, such as ammonium and potassium hydroxides, may be used for neutralization of the sulfuric acid solution. Similarly, a number of solvents other than chloroform may be used for extraction purposes, such as carbon tetrachloride, trichlorethylene, tetrachlorethylene, benzene, toluene, etc.

There is a marked increase in temperature when cyclohexanone oxime is added to cold concentrated sulfuric acid. Should the temperature be raised sufficiently in this manner, the rearrangement would take place, but, because of the large amount of oxime rearranging, the reaction would be explosive, and characterized by a sudden rise in temperature with consequent charring and low yield of lactam. Similarly, when a small quantity of oxime is dissolved in sulfuric acid with cooling and the resulting solution then heated cautiously over a free flame—the usual method for conducting the Beckmann rearrangement—the reaction is sudden and violent and accompanied by charring.

By the method of this invention, however, large amounts of oxime may be safely rearranged in a short time. Since the temperature of the reaction is lower than that of the uncontrolled reaction, the charring action of sulfuric acid is minimized and the yields are correspondingly high.

The threshold temperature is the temperature below which the reaction does not take place. At the threshold temperature, when an oxime is added to the sulfuric acid the exothermic rearrangement reaction of the oxime to the corresponding lactam takes place. Below this temperature, however, the rearrangement reaction does not take place. The threshold temperature varies with the concentration of the acid and the particular oxime added.

Since many apparently and widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that the invention is not to be limited to the specific embodiments thereof, except as defined in the following appended claims.

I claim:

1. The process for the production of lactams which comprises heating sulfuric acid of a concentration in excess of 75% to a temperature within the range of about 90° C. to about 130° C. then adding a cyclic ketoxime to said sulfuric acid in such portions and at such a rate that the temperature is maintained within the range recited by the heat of the reaction.

2. The process in accordance with claim 1 characterized in that the cyclic ketoxime is cyclohexanone oxime.

3. The process for the production of caprolactam which comprises heating a sulfuric acid of a concentration of substantially 90 to 96% to a temperature of substantially 90° to 95° C., then adding cyclohexanone oxime to said sulfuric acid in such proportions and at such a rate that the

temperature is maintained within the range recited by the heat of reaction.

4. The process for the production of lactams which comprises heating sulfuric acid of a concentration in excess of 75% to a temperature above the threshold temperature for the rearrangement of cyclic ketoximes to lactams, and then adding cyclic ketoxime to said sulfuric acid in such proportions and at such a rate that the temperature is maintained near said temperature to which the sulfuric acid is heated.

5. The process in accordance with claim 1 characterized in that the cyclic ketoxime is an alicyclic ketoxime.

6. The process in accordance with claim 1 characterized in that the cyclic ketoxime is a hydrocarbon substituted alicyclic ketoxime.

7. The process in accordance with claim 1 characterized in that the cyclic ketoxime is an alkyl substituted alicyclic ketoxime.

8. The process for the production of caprolactam which comprises heating sulfuric acid of the concentration of substantially 96% to a temperature within the range of 90° to 100° C., then adding cyclohexanone oxime to said sulfuric acid in such proportions and at such a rate that the temperature is maintained within the range recited by the heat of reaction.

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