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PREPARATION OF ALIPHATIC CARBOXYLIC ACID AMIDES FROM SATURATED ALIPHATIC HYDROCARBONS

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This invention relates to the preparation of aliphatic carboxylic acid amides from saturated aliphatic hydrocarbons under the conditions of the Willgerodt reaction.

In 1887 Willgerodt discovered that aryl alkyl ketones react at high temperatures and under pressure with yellow ammonium polysulfide to form crystalline nitrogenous materials. The following year he reported that these products were amides of the aryl-substituted aliphatic acids containing the same number of carbon atoms as the starting ketones, accompanied by the ammonium salts of these acids. In subsequent years Willgerodt extended the reaction to a large number of different aryl alkyl ketones. Since that time the Willgerodt reaction has been applied to a large number of other organic compounds, and up to the present time the following types of compounds are known to react under the conditions of the Willgerodt reaction to give carboxylic acids and derivatives thereof having the same number of carbon atoms as the organic compound from which they are formed: dialkyl ketones, aralkyl alkyl ketones, cycloalkyl ketones, alicyclic ketones, aliphatic alcohols, aliphatic organic halides, aldehydes, thioaldehydes, olefins, aliphatic and aromatic substituted olefins, acetylenes and aliphatic and aromatic substituted acetylenes.

An object of the present invention is to extend the Willgerodt reaction to saturated aliphatic hydrocarbons. A further object of the present invention is to provide a method of preparing aliphatic carboxylic acid amides from saturated aliphatic hydrocarbons. Other objects will be apparent from the description of the invention given hereinafter.

The above objects are accomplished according to the present invention by heating together a saturated aliphatic hydrocarbon with a mixture comprising essentially sulfur and ammonia at a temperature in excess of 300° C.

More specifically, the present invention comprises heating together a saturated aliphatic hydrocarbon containing from 3 to 8 carbon atoms per molecule, with a mixture comprising essentially sulfur and ammonia at a temperature between 300° C. and 360° C. In one of the embodiments of the invention, water is employed as a reactant, and aqueous ammonium polysulfide is present in the reaction mixture. The present invention thus provides a novel method for preparing amides, by reaction between an alkane and aqueous ammonium polysulfide.

The present invention resides primarily in the discovery that saturated aliphatic hydrocarbons will react under the conditions of the Willgerodt reaction to give aliphatic carboxylic acid amides. Heretofore, certain unsaturated aliphatic hydrocarbons have been converted to corresponding amides, but it was not known that the herein considered saturated aliphatic hydrocarbons could be converted in this manner and, thus, a practical method of obtaining certain aliphatic carboxylic acid amides has been provided where such amides could only be prepared with great difficulty, if at all heretofore.

The conditions, in general, of the Willgerodt reaction are known and are applicable in the present invention

except that the temperature range herein specified should be observed. That is, the reaction is normally conducted in a closed container under pressure to prevent loss of volatiles. It may be run under anhydrous conditions or in the presence of water. Originally, Willgerodt used yellow ammonium polysulfide, but it has since been found that a mixture of ammonia and sulfur can be used regardless of whether it is ammonium polysulfide or, literally, simply a mixture of sulfur with ammonia. It is practical and expedient to use as the Willgerodt reagent simply powdered sulfur added to ammonia, either aqueous or anhydrous, although it is to be understood that in defining the reagent herein as comprising essentially sulfur and ammonia, the polysulfide form of the Willgerodt reagent is included, the present invention in its broader phase not being concerned with specific variations of the Willgerodt reagent.

The following examples in which all parts are given by weight unless otherwise specified, illustrate specific embodiments of the invention.

Example I

The following reaction was carried out in a 500 milliliter stainless steel hydrogenation bomb equipped with iron gaskets. Agitation of the bomb was accomplished by placing the bomb in a rocker assembly equipped with band heaters.

A mixture of 15 parts of isobutane (0.258 mol), 35 parts of sulfur (1.1 mols) and 68 parts of concentrated aqueous ammonia (28% ammonia) (1.1 mols) was introduced into the bomb and the mixture was agitated for a period of two hours at a temperature ranging between 320° C. and 333° C. The initial pressure was about 2625 pounds per square inch and rose to about 3425 pounds per square inch.

On cooling to room temperature the resulting product contained some crystals. The whole mixture was extracted continually with ether for 16 hours. The dried ether extract yielded 5 parts of crude isobutyramide on evaporation. Further recrystallization gave a white crystalline product melting at 117° C. and containing 15.9% nitrogen (isobutyramide: m. p. equals 125° C., 16.1% nitrogen). The above yield of isobutyramide represents 21.4%.

Example II

The following reaction was carried out in the same type bomb used in Example I.

A mixture of 15 parts of propane (0.320 mol) containing less than 0.6% unsaturates, 35 parts of sulfur (1.1 mols), and 68 parts of concentrated aqueous ammonia (28% ammonia) (1.1 mols) was introduced into the bomb, and the mixture was agitated for a period of two hours at a temperature ranging between 335° and 345° C.

A continuous ether extraction of the resulting product led to the isolation of a small amount of solid material. Fractional crystallization from ether and ethyl acetate gave two fractions of material. The higher melting fraction was identified as at least 90% acetamide by infrared analysis. The lower melting fraction (liquid at room temperature) contained the C=O band in the infrared and was identified as formamide.

The reaction liquid after the above ether extraction was acidified and filtered free of precipitated sulfur. The acidified mix was again extracted continuously with ether for 16 hours. On evaporation of the ether, an acidic residue was obtained which appeared to be mainly formic and acetic acids.

The above results with propane suggest a cleavage of carbon to carbon bonds during the course of the reaction. Literature dealing with the mechanism of the Willgerodt reaction makes a point of the fact that the subject reaction never rearranges or alters the carbon

skeleton. However, prior to the present invention the subject saturated aliphatic hydrocarbons had not been subjected to the conditions of the Willgerodt reaction. In general, experience has shown that the various amides and other products obtained by the reaction of the present invention can be altered by varying the reaction conditions and the proportions of the reactants. When a greater proportion of the saturated aliphatic hydrocarbon was used, more of the amide of the original starting material was formed and lesser amounts of degradation products are obtained.

It is to be understood that the foregoing examples are merely illustrative, and the present invention broadly comprises heating together a saturated aliphatic hydrocarbon with a mixture comprising essentially sulfur and ammonia, at a temperature in excess of 300° C.

When applied to the saturated aliphatic hydrocarbons of the present invention, the Willgerodt reaction may be carried out under substantially anhydrous conditions or in the presence of water. When substantially anhydrous conditions prevail, the carboxylic acid derivative resulting is a thioamide. These thioamides contain the group —$CSNH_2$. When water is present, the corresponding amide which is obtained contains the group —$CONH_2$.

Depending upon the end product desired, the reaction may be carried out in the presence of inert solvents either in the presence of water or under substantially anhydrous conditions. The use of a suitable solvent such as dioxane, pyridine or benzene may facilitate preparation of the desired end product from the reaction liquors. Furthermore, such inert solvents may be used to render complex mixtures of reactants homogeneous and reduce the total vapor pressure of the heated reaction mass.

In addition to the saturated aliphatic hydrocarbons disclosed in the foregoing examples, the following specific hydrocarbons may be reacted according to the process of the present invention to produce various derivatives of aliphatic carboxylic acids, particularly, aliphatic carboxylic acid amides and thioamides. Included among such saturated aliphatic hydrocarbons are butane; pentane; 2,2-dimethyl butane; 2,3-dimethyl butane; 2,2-dimethyl pentane; 2,3-dimethyl pentane; hexane; 2-methyl hexane; heptane and octane.

The products resulting from treating the herein described saturated aliphatic hydrocarbons according to the present process may be one or more of the following: salts of carboxylic acids, having the grouping —$COONH_4$; amides of carboxylic acids, having the grouping —$CONH_2$; thioamides, having the grouping —$CSNH_2$; thioacids having the grouping —CSSH; and salts of thioacids having the grouping —$CSSNH_4$.

As the reaction temperature is increased, the rate of reaction increases, but the severity of degradation of the starting material increases and cleavage of carbon to carbon bonds will occur. Hence, the particular reaction temperature selected in any given case will be dependent upon the particular starting material and the particular products or the particular ratio of the end products desired. Furthermore, the time of the reaction also influences the ratio of the yields, the longer the reaction time the greater the changes are that carbon to carbon cleavage will take place. Because elevated temperatures are required for the Willgerodt reaction, the reaction is carried out in a closed system to avoid loss of reactants from the reaction medium by vaporization. Consequently, in the absence of applied pressure, the pressure of the system will vary with the temperature of the reaction and the volatility of the reactants or the reaction medium. For the process of the present invention, it is recommended that a temperature in excess of 300° C. be used, preferably from 300° to 360° C.

The proportion of saturated aliphatic hydrocarbons to the other reactants may be varied widely. To obtain good yields of carboxylic acid amides, a slight excess of ammonia is required over that which is chemically equivalent to the amount of hydrocarbon. For example, ammonia concentrations of 1.5 mols per mol of hydrocarbon have given good yields of amides. Theoretically, only 1 mol of ammonia per mol of hydrocarbon would be required.

The amount of sulfur to be used should be as low as possible in most instances to decrease the probability of side reactions and increase the ease of processing the mixture or reaction products. It has been found that the reaction proceeds rapidly with good yields in the presence of an amount of sulfur in excess of that chemically equivalent to the amount of hydrocarbon, that is, in excess of about 2 mols of sulfur per mol of hydrocarbon. The preferred amount of sulfur ranges from about 2 to 5 mols per mol of hydrocarbon.

When the reaction is carried out in the presence of water, the lower limit on water concentration is mainly dependent on the amount necessary to give the optimum yield of carboxylic amide, that is convert any thioamide to carboxylic amide, and the amount necessary to facilitate handling the liquid reaction product. For example, 1 mol of water is necessary to react with 1 mol of of the hydrocarbon, and at least 1 additional mol of water is necessary to prevent formation of a thioamide and other by-products and also contribute to making the reaction products sufficiently liquid to maintain the solid reactants and products in solution. The use of less than about 2 mols of water per mol of hydrocarbon results in the formation of appreciable amouts of thioamide, other by-products, and excessive amounts of degradation products. Furthermore, a water concentration below 2 mols per mol of hydrocarbon makes handling of ammonium hydrosulfide formed difficult and thereby complicates the recovery process. On the other hand, a water concentration above about 6 mols per mol of hydrocarbon contributes an excessive volume of liquid to be processed. The optimum amount of water recommended for the present process ranges from about 2 to 6 mols per mol of hydrocarbon.

From the foregoing, it will be appreciated that the proportions of reactants present may be varied, as the reaction will take place in the presence of any appreciable amounts of the reactants, merely the rate of the reaction and the approach of the yield to theoretical being affected as proportions are varied. Further, the considerations with respect to the proportions are equally applicable whether a mixture of sulfur and ammonia is used or yellow ammonium polysulfide. Small amounts of hydrogen sulfide, up to 1 mol per mol of hydrocarbon, may be added initially to the mixture of ammonia and sulfur to dissolve the sulfur and promote the rapid formation of a homogeneous reaction solution. This is not necessary, however, because hydrogen sulfide is formed in the reaction and ammonium polysulfide is formed with the ammonia and sulfur present.

I claim:

1. A process for preparing alkanoic amides which comprises introducing an alkane having from 3 to 8 carbon atoms per molecule, sulfur, water and ammonia into a pressure-resistant vessel, and thereafter heating the resultant mixture under superatmospheric pressure at a temperature in the range of 300° C. to 360° C., whereby alkanoic amide formation occurs, and separating from the resulting mixture the said alkanoic amide thus produced.

2. A process for preparing amides of alkanoic acids which comprises heating an alkane having from 3 to 8 carbon atoms per molecule with liquid aqueous ammonium polysulfide, the quantity of water present initially being 2 to 6 mols per mol of alkane, at a temperature within the range of 300° C. to 360° C., whereby carboxylic amide formation occurs, and thereafter separating from the resulting mixture the amide produced by the ensuing reaction.

3. The process of claim 2 in which the said alkane is isobutane.

4. A process for preparing acetamide and formamide which comprises heating propane with liquid aqueous ammonium polysulfide, the quantity of water present initially being from 2 to 6 mols per mol of propane, at a temperature within the range of 300° to 360° C., in a pressure-resistant vessel, whereby a mixture of acetamide and formamide is obtained, and thereafter separating the said acetamide and the said formamide from the resulting mixture.

5. A process which comprises introducing isobutane, sulfur, water and ammonia into a pressure-resistant vessel, and thereafter heating the resultant mixture under superatmospheric pressure at a temperature in the range of 300° C. to 360° C., whereby alkanoic amide formation occurs, and separating from the resulting mixture the said alkanoic amide thus produced.

6. A process which comprises introducing propane, sulfur, water and ammonia into a pressure-resistant vessel, and thereafter heating the resultant mixture under superatmospheric pressure at a temperature in the range of 300° C. to 360° C., whereby alkanoic amide formation occurs, and separating from the resulting mixture the said alkanoic amide thus produced.

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