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PROCESS FOR MAKING HYDROXAMIC ACIDS

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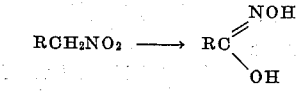
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6 Claims. (Cl. 260—500)

My invention relates to the production of hydroxamic acids from primary nitrohydrocarbons.

The primary nitrohydrocarbons may be obtained according to a number of different reactions, but are most economically prepared by vapor phase nitration of saturated hydrocarbons in accordance with the process of U. S. Patent No. 1,967,667 by H. B. Hass, E. B. Hodge, and B. M. Vanderbilt. The nitroparaffins produced by this process from petroleum hydrocarbons constitute an advantageously cheap source of aliphatic compounds for the production of organic chemicals. I have now found that hydroxamic acids may be produced from these nitro compounds with satisfactory yields and conversions by the reaction of the nitrohydrocarbons with strong acids under the controlled conditions as hereinafter set forth.

It has been shown in my copending U. S. Serial Numbers 148,107, 148,108 and 148,109, filed June 14, 1937, that carboxylic acids may be readily prepared by the reaction of primary nitrohydrocarbons with strong acids under certain conditions. I have now discovered that under certain different well defined conditions the treatment of the same nitro compound with a strong acid will unexpectedly give rise to the production of the corresponding hydroxamic acid as a major product. The process of my present invention may be briefly described as comprising subjecting the primary nitrohydrocarbon at a temperature substantially under 120° C. to the action of a strong acid in the complete or almost complete absence of water. The reaction which takes place may be represented as follows:



The strong acid utilized as the converting agent apparently enters into the reaction in an intermediate stage, but may be recovered at the conclusion of the reaction, and from this standpoint may be considered as a catalyst.

The nitrohydrocarbons which are suitable for my process are the primary nitroparaffins, the cycloalkyl and aryl substituted primary nitroparaffins, and the like. The primary nitroparaffins are very satisfactory for my process, and among these nitroethane, 1-nitropropane, 1-nitrobutane and 1-nitro-2-methylpropane are particularly suitable. It is to be understood however, that my invention is not to be limited to any particular nitrohydrocarbon of this series but is generally applicable to all nitrohydrocarbons containing the group —CH_2—NO_2.

The acids which may be used to effect the conversion of the nitrohydrocarbons to hydroxamic acids in my process may be any acids having dissociation constants in excess of 10^{-2}. The term "acid", in this connection, signifies any acid having a mineral acid grouping or a carboxylic acid grouping. Among such acids may be mentioned sulfuric, phosphoric, dichloracetic, oxalic, benzene sulfonic, p-toluene sulfonic, and beta-naphthalene sulfonic acids. It will be evident, of course, that although any acid having a dissociation constant in excess of the specified value will serve to effect the conversion of the nitro compound into the corresponding hydroxamic acid, some of these acids will be less advantageous than others. The acid employed should preferably be neither strongly oxidizing nor strongly reducing, in order to minimize any tendency for decomposition of the hydroxamic acid. For this reason nitric acid and other similar strongly oxidizing acids may be considered as excluded from the above definition of acids which may be employed in my process. It will also be apparent that certain of these acids will be more advantageous than others in respect to their removal from the final reaction mixture. From these standpoints, as well as from the cost standpoint, I prefer to employ sulfuric acid. However, it is to be understood that my invention is not limited to the use of this or any of the other acids specifically mentioned.

I have found that the reaction will occur over a wide range of ratios of acid to nitrohydrocarbon, but that preferably at least 1 mole of acid per mole of nitrohydrocarbon should be employed. The optimum ratio may in any particular case be readily determined by simple preliminary experiments.

The reaction temperature is preferably kept below 120° C. since at higher temperatures the hydroxamic acid tends to decompose. However, the optimum temperature may vary widely for each reaction and the various concentrations of acid used.

I have found that for satisfactory yields of hydroxamic acids only minimal concentrations of water should be present in the reaction mixture, especially when the reaction is carried out at elevated temperatures. I prefer, therefore, to employ anhydrous acids as the converting acids, although slightly less concentrated acids may be employed with resulting lower yields of hydroxamic acids. Although water should be present in only minimal concentrations during the main reaction, I have found that for optimum yields

water may be required at the conclusion of the reaction to complete the conversion of intermediate products to the hydroxamic acid stage. In such cases, the contact with water should not be unduly prolonged and should take place only at low temperatures. The introduction of water in the final recovery operations will usually be sufficient to accomplish this end.

My invention may be illustrated by the following examples:

Example I

Fifty-eight parts by weight of 95% sulfuric acid were dropped into 50.5 parts of cold 1-nitropropane and the resulting mixture was allowed to stand at room temperature. After nine days, a 12% conversion to propionohydroxamic acid was obtained.

Example II

A mixture of 101 parts by weight of 1-nitropropane and 110 parts of 100% sulfuric acid was allowed to stand at room temperature for 27 days. Propionohydroxamic acid was recovered from the reaction mixture corresponding to a 35% conversion to the crude product.

Example III

A mixture of 101 parts by weight of 1-nitropropane and 110 parts of 100% sulfuric acid was maintained at 37° C. for ten days. At the end of this time, analysis of the reaction mixture indicated 30% conversion of the nitropropane to propionohydroxamic acid.

Example IV

A mixture of 101 parts by weight of 1-nitropropane and 110 parts of 100% sulfuric acid was maintained at a temperature of 80 to 100° C. for 20 hours. Propionohydroxamic acid was recovered from the reaction mixture corresponding to a 44% conversion into the crude product.

The hydroxamic acid may be isolated from the resulting solution by any suitable procedure. I have found the following to be satisfactory for the isolation of propionohydroxamic acid from a reaction mixture utilizing sulfuric acid as the converting acid. After the reaction is complete, the mixture is cooled and poured into ice water. While cold, the sulfuric acid is neutralized by adding powdered calcium carbonate, and the resulting calcium sulfate is then filtered off. The filtrate is concentrated at reduced pressure, the temperature varying from about 40 to 60° C., refiltered and concentrated to a thick syrup. This syrup will then crystallize to a crude product on seeding with a few propionohydroxamic crystals. The crude hydroxamic crystals may be readily purified by recrystallization from a suitable solvent. It is to be understood that my invention is in no way to be limited to the method for obtaining the hydroxamic acid from the reaction mixture. The foregoing method is only an example of how this may be done.

It is also to be understood, of course, that the above examples are illustrative only, and my inventtion is not to be construed as limited to the particular materials or procedures set forth. Numerous modifications of procedure will naturally occur to those skilled in the art, and my invention includes any such modifications or the use of any obvious equivalents.

My invention now having been described, what I claim is:

1. A process for the production of hydroxamic acids from primary nitrohydrocarbons which comprises subjecting the nitrohydrocarbon to the action of an acid having a dissociation constant in excess of 10^{-2} and which is not strongly oxidizing in character, the reaction being effected in the presence of minimal concentrations of water.

2. A process for the production of hydroxamic acids from primary nitrohydrocarbons which comprises subjecting the nitrohydrocarbon to the action of an acid having a dissociation constant in excess of 10^{-2} and which is not strongly oxidizing in character, the reaction being effected in the absence of water.

3. A process for the production of hydroxamic acids from primary nitrohydrocarbons which comprises subjecting the nitrohydrocarbon to the action of an acid having a dissociation constant in excess of 10^{-2} and which is not strongly oxidizing in character, at a temperature from about room temperature to about 120° C. and in the absence of water.

4. A process for the production of hydroxamic acids from primary nitroparaffins which comprises subjecting the nitroparaffin to the action of sulfuric acid at a temperature from about room temperature to about 120° C. in the absence of water.

5. A process for the production of hydroxamic acids from primary nitroparaffins which comprises subjecting the nitroparaffin to the action of phosphoric acid at a temperature from about room temperature to about 120° C. in the absence of water.

6. A process for the production of hydroxamic acids from primary nitroparaffins which comprises subjecting the nitroparaffin to the action of benzene sulfonic acid at a temperature from about room temperature to about 120° C. in the absence of water.

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