

# UNITED STATES PATENT OFFICE

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## SYNTHESIS OF IMINODIACETONITRILE

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1

This invention relates to the synthesis of nitriles and particularly a new method for preparing iminodiacetonitrile,  $\text{HN}(\text{CH}_2\text{CN})_2$ .

Iminodiacetonitrile has been prepared heretofore by reaction between hexamethylenetetramine and hydrogen cyanide, but the process has been unsatisfactory and wasteful because of the poor yield of imododiacetonitrile obtained, and because the reaction is so slow that it requires several days for completion.

It has also been disclosed heretofore [Polstorff and Meyer, Ber. 45, 1905-12 (1912)] that in the synthesis of nitrilotriacetic acid by reaction between potassium cyanide and aqueous formaldehyde, minor amounts of potassium iminodiacetate are produced. Poldorff and Meyer have attempted to explain the formation of potassium iminodiacetate by postulating that under the alkaline conditions prevailing a reaction may take place between amino-acetonitrile and formaldehyde cyanhydrin to form iminodiacetonitrile which may then react with the alkali to form the salt of iminodiacetic acid. The said postulated process, however, has not been useful for the synthesis of iminodiacetonitrile.

An object of this invention is to provide a process whereby iminodiacetonitrile may be prepared without appreciable loss of nitrile. Another object is to provide a process for the manufacture of iminodiacetonitrile which produces the said nitrile substantially free from contamination by other materials such as nitrilotriacetonitrile.

These and other objects are accomplished in accordance with this invention by reacting aminoacetonitrile with formaldehyde cyanhydrin at a temperature of about 50° C. to 150° C., in the absence of alkali (i. e., alkaline materials such as hydroxides, carbonates, cyanides, etc. of the alkali metals, alkaline earth metals and the like), the initial molal ratio of aminoacetonitrile to formaldehyde cyanhydrin being about 1:0.3 to 1:1.5. In contrast with the postulated process of Poldorff and Meyer, it has been discovered in accordance with this invention that, at slightly elevated temperatures, aminoacetonitrile and formaldehyde cyanhydrin, in the presence of alkali, are rapidly (and sometimes violently) decomposed, so that it is essential in the practice of this invention to eliminate any traces of alkaline catalysts. One method for accomplishing this result is to add to the reaction mixture about 0.001 to 0.5% of a mineral acid stabilizer, based on the initial weight of the formaldehyde cyanhydrin. The presence of the said mineral acid stabilizer is not indispensably necessary in the

2

practice of the invention, provided, of course, that care is taken to avoid the presence of even small traces of alkali. The invention, therefore, contemplates the synthesis of iminodiacetonitrile by heating aminoacetonitrile with formaldehyde cyanhydrin in the aforesaid molal proportions, but preferably in about equimolar quantities, in the absence of alkaline catalysts.

In a specific embodiment, the present invention contemplates the synthesis of iminodiacetonitrile by heating substantially equimolar quantities of aminoacetonitrile and formaldehyde cyanhydrin at a relatively high temperature within the aforesaid range, whereby a rapid reaction between aminoacetonitrile and formaldehyde cyanhydrin takes place without excessive decomposition of the reactants, thus producing iminodiacetonitrile in very good yield. Therefore, in a preferred method of practicing the invention, the said reactants are heated at a temperature of about 140° C., in the absence of alkali, whereby a reaction producing iminodiacetonitrile takes place. Decomposition due to prolonged heating is prevented by stopping the reaction after a total reaction time not exceeding about 15 minutes, preferably by quickly cooling the mixture. Under the aforesaid preferred conditions, only a small quantity of tarry by-product resulting from the decomposition of the constituents of the reaction mixture is produced. The temperature range within which this rapid reaction takes place without the formation of excessive quantities of decomposition products is somewhat narrow, preferably about 135° C. to 150° C.

The aminoacetonitrile used as one of the reactants in accordance with this invention may be prepared by heating formaldehyde cyanhydrin with anhydrous ammonia, or by any other suitable process. While pure aminoacetonitrile may be used, it is frequently convenient to employ aminoacetonitrile in the form of an aqueous solution. Similarly, the formaldehyde cyanhydrin employed in the practice of the invention is preferably anhydrous formaldehyde cyanhydrin which may be prepared by reacting formaldehyde with hydrogen cyanide and distilling the resulting mixture in the presence of an acidic stabilizer at diminished pressures. If desired, aqueous solutions of formaldehyde cyanhydrin may be employed in place of the purified formaldehyde cyanhydrin. Moreover, the formaldehyde cyanhydrin may be formed in situ from formaldehyde and hydrogen cyanide in the presence of an acid-reacting substance. The acid-reacting materials in general are suitable as stabilizers for the react-

3

ants employed in the practice of the invention, the preferred stabilizers being mineral acids, particularly phosphoric acid.

In one manner of carrying out the invention, the formaldehyde cyanhydrin and aminoacetonitrile are mixed together and heated in a flask for the required reaction time, and the resulting mixture is thereafter chilled whereby the iminodiacetonitrile separates therefrom in the form of crystals.

The invention may be illustrated further by means of the following examples:

*Example 1.*—A mixture containing 17.1 grams of aminoacetonitrile and 5.8 grams of formaldehyde cyanhydrin (containing a few drops of phosphoric acid per liter) was heated on the steam bath at a temperature of about 100° C. for one hour. The resulting mixture was cooled by means of an ice bath whereby crystals of iminodiacetonitrile were deposited. The yield of iminodiacetonitrile was about 70% of the theoretical.

*Example 2.*—The mixture containing 58 grams (one mol) of formaldehyde cyanhydrin and 57 grams (one mol) of aminoacetonitrile was heated together in a flask by means of an oil bath until the reaction mixture reached a temperature of 140° C. After about 5 minutes, a vigorous reaction took place with evolution of hydrogen cyanide and water. The reaction mixture was maintained at a temperature of 140° C. for a total reaction time of 15 minutes. Upon cooling, the product crystallized forming a reddish brown solid. Four such runs were made, after which the crude products were combined and iminodiacetonitrile was separated therefrom by extraction with hot benzene until only a brown resinous material remained. The iminodiacetonitrile crystallized from the benzene on cooling in long, colorless needles. These were removed by filtration and dried. The total weight of iminodiacetonitrile thus obtained was 296 grams, which corresponds to a yield of about 78%.

It is evident that numerous changes may be made in the manner of conducting the reaction between aminoacetonitrile and formaldehyde cyanhydrin without departing from the scope of this invention. For example, the reaction may be carried out in a closed pressure-resisting vessel, and at pressures higher than atmospheric. The reaction heat may be dissipated through cooling coils, water-jackets, or other convenient means. In embodiments in which an acidic stabilizer is employed, the stabilizer may be removed in the form of an insoluble salt prior to isolating the product, if desired. While in the examples the invention is illustrated by means of batchwise operation, it is to be understood that excellent results also are obtained in continuous operation. In the continuous process, tubular converters, within which the reactants are heated at controlled short reaction times,

4

give outstanding results. Any convenient method may be employed for separating iminodiacetonitrile from the crude reaction product, such as crystallization from any of the common organic solvents.

Since many different embodiments of the invention may be made without departing from the spirit and scope thereof, it is to be understood that I do not limit myself except as set forth in the following claims.

I claim:

1. A process for the synthesis of iminodiacetonitrile which comprises heating aminoacetonitrile with formaldehyde cyanhydrin at a temperature of about 100° to 150° C., in the presence of about 0.001 to 0.5% of a mineral acid stabilizer based on the initial weight of the formaldehyde cyanhydrin, the initial molal ratio of aminoacetonitrile to formaldehyde cyanhydrin being about 1:0.3 to 1:1.5, and thereafter separating iminodiacetonitrile from the resulting mixture.

2. The process set forth in claim 1, in which the said mineral acid stabilizer is phosphoric acid.

3. A process for the synthesis of iminodiacetonitrile which comprises heating a reaction mixture consisting of aminoacetonitrile and formaldehyde cyanhydrin in equimolar proportions at a temperature of about 135° to 150° C., whereby a reaction producing iminodiacetonitrile takes place, maintaining the resulting reaction mixture at the said reaction temperature for a total reaction time not exceeding about 15 minutes, and thereafter cooling the resulting mixture and separating iminodiacetonitrile therefrom.

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