

UNITED STATES PATENT OFFICE

2,257,814

PREPARATION OF OMEGA-AMINO NITRILES

George Wayne Rigby, Wilmington, Del., assignor
to E. I. du Pont de Nemours & Company, Wil-
mington, Del., a corporation of Delaware

No Drawing. Application May 2, 1940,
Serial No. 332,961

6 Claims. (Cl. 260-464)

This invention relates to a catalytic process and, more particularly, it relates to the catalytic hydrogenation of dinitriles. More specifically this invention relates to the partial hydrogenation of aliphatic dinitriles in the presence of mild-acting, selective, cobalt-containing catalysts to omega-amino aliphatic nitriles.

In my copending application Serial No. 231,507, filed September 24, 1938, now U. S. Patent No. 2,208,598, issued July 23, 1940, of which this is a continuation-in-part, there is described a process for the production of long-chain omega-amino aliphatic nitriles in which an aliphatic dinitrile having at least four carbon atoms in contiguous relation between the nitrile groups is subjected to partial hydrogenation under carefully controlled conditions of temperature and pressure in the presence of anhydrous ammonia, and preferably using a finely divided metallic nickel hydrogenation catalyst. According to the preferred embodiments of this invention, the reaction is stopped when the amount of hydrogen taken up corresponds to approximately one-half the quantity required for complete hydrogenation of both nitrile groups. On working up the mixture there are obtained as the major products of the reaction the omega-aminonitrile and the aliphatic diamine corresponding in chain length to the original dinitrile. Adiponitrile, for example, will yield about 50 per cent of epsilon-aminocapronitrile and 10 to 15 per cent of hexamethylenediamine, both of which are valuable chemical products. The remainder of the adiponitrile is converted largely to high boiling polymeric products.

From practical considerations the success or failure of a chemical process in large scale operation will often depend solely on yield performance. By this it is not meant that high yields of a single product are essential for a process to be commercially feasible, but rather that the total yield of one or more useful products must exceed a certain definite minimum level which for any given process is determined by costs of starting materials, operation, equipment, refining and other similar factors. Accordingly, in the above-mentioned partial hydrogenation process a yield loss corresponding to as much as 30 to 40 per cent of the starting material constitutes a serious handicap to economical operation on a commercial scale, not only because the low weight yield is accompanied by increased raw materials requirement but also because the formation of large amounts of tarry by-products hampers the refining process and may even affect adversely the quality of the desired products.

It has now been found that these disadvantages can be overcome by using finely divided, selective, mild-acting cobalt-containing catalysts in the partial hydrogenation process. For example, with a suitable cobalt-containing catalyst adiponitrile can be smoothly hydrogenated under carefully controlled conditions to give a combined yield of epsilon-aminocapronitrile and hexamethylenediamine amounting to 85 to 90 per cent of theory instead of 60 to 65 per cent, as in the prior process. This invention accordingly provides for the first time an improved, sound, practicable process for the manufacture of omega-aminonitriles from the corresponding aliphatic dinitriles, and the discovery thereof comprises a novel and important contribution to the art of catalytic hydrogenation.

It is an object of this invention to provide a commercially practical method for converting aliphatic dinitriles having at least 4 carbon atoms in contiguous relationship between the nitrile groups to the corresponding aminonitriles. Another object is to provide a simple and direct method for producing omega-aminocapronitrile. Other objects will be apparent from the following description of this invention.

According to this invention, aliphatic dinitriles containing at least four carbon atoms in contiguous relation between the nitrile groups are brought into contact with hydrogen in the presence of anhydrous ammonia and mild-acting selective cobalt-containing hydrogenation catalysts at elevated temperatures and pressures. The rate and extent of hydrogen absorption is controlled so that the major product of the reaction is the corresponding omega-amino aliphatic mononitrile.

Aliphatic dinitriles containing at least four carbon atoms in contiguous relation between the nitrile groups are converted to omega-aminonitriles by the following general procedure:

100 parts by weight of an aliphatic dinitrile, approximately 75 parts by weight of anhydrous ammonia, and 3 to 10 parts by weight of a mild-acting selective cobalt-containing hydrogenation catalyst are charged into a high pressure reaction vessel provided with means of heating and agitation. The mixture is treated with hydrogen under pressures in the range from 1500 to 3000 lbs./sq. in. at temperatures preferably in the range of 100° to 140° C. Under these conditions hydrogen is absorbed smoothly, and fresh amounts are added from time to time to maintain the reaction pressure within the operating range. When approximately 40 to 70 per cent

of the amount of hydrogen theoretically required to convert the dinitrile to a diamine has been absorbed, the reaction is stopped and the charge removed from the reaction vessel. The catalyst is separated by filtration and the crude product refined by vacuum fractional distillation. There is obtained 30 to 40 parts by weight of the corresponding aliphatic diamine and 50 to 68 parts by weight of an aliphatic omega-aminonitrile corresponding in chain length to the original dinitrile. The total yield of useful products from the reaction usually amounts to 85 to 90 per cent of theory, based on the amount of dinitrile employed as starting material.

The preferred embodiments and advantages of the invention are illustrated by the following selected examples. Parts are by weight, unless otherwise specified.

Example I

A mild-acting cobalt-containing hydrogenation catalyst was prepared according to the following procedure.

An alloy containing 60 parts of aluminum, 38 parts of iron, and 2 parts of cobalt was prepared and ground to a fine powder, most of which passed 325 mesh. 227 parts of the finely ground powder was suspended in 1000 parts of water and the mixture brought to the boiling point with stirring. To the stirred mixture was added slowly a solution containing 227 parts of sodium hydroxide and 500 parts of water. After a small amount of the caustic solution had been added, a vigorous reaction ensued which continued exothermically for 20 to 30 minutes without further addition of alkali. The remainder of the caustic solution was added at a more rapid rate during about 1 hour, after which the mixture was boiled with stirring for an additional 3 to 4 hours. The solid material was allowed to settle, the supernatant caustic liquid decanted, and the sludge washed twice with water. The resulting finely divided material was resuspended in a solution containing 227 parts of sodium hydroxide in 1500 parts of water and boiled for 4 hours. The catalyst was again allowed to settle, the supernatant liquid decanted as before, and the residue washed thoroughly with water until the washings were neutral to litmus. Finally, the sludge was washed with alcohol until essentially free from water and stored under absolute alcohol. The finely divided catalyst obtained by this process contained approximately 95 parts by weight of iron and 5 parts by weight of cobalt.

100 parts of pure adiponitrile, 75 parts of anhydrous ammonia, and 10 parts of the iron-cobalt catalyst prepared as described above were charged into a high pressure reaction vessel equipped with a stirring device. Hydrogen under pressure was admitted until the total pressure was within the range of 2000 to 3000 lbs./sq. in. and the vessel and its contents heated to 120° C. Under these conditions hydrogen was absorbed smoothly. The reaction was continued until approximately 50 per cent of the theoretical amount of hydrogen had been taken up. At this point the reaction was stopped and the charge removed from the reaction vessel. After filtering from the catalyst, the crude product was refined by vacuum fractional distillation. There was obtained 1.9 per cent of hexamethylenimine, B. P. 135° C.; 6.4 per cent of hexamethylenediamine, B. P. 105° C./27 mm.; 68 per cent of epsilon-aminocapronitrile, B. P. 131° C./30 mm.; and 24.8 per cent of high boiling residue

consisting mainly of unreacted adiponitrile. Excluding adiponitrile from the residue, 74.4 per cent of the starting material was converted to useful materials.

Example II

A mixture of 100 parts of pure adiponitrile, 8 parts of cobalt-on-kieselguhr catalyst, and 75 parts of anhydrous ammonia was charged into a hydrogenation autoclave and treated with hydrogen at pressures between 2000 and 3000 lbs./sq. in. at 120° C. Under these conditions approximately 70 per cent of the theoretical amount of hydrogen was absorbed during 0.9 hour. The product was isolated as described in Example I, and on vacuum fractional distillation there was obtained 2.4 parts by weight of hexamethylenimine, 42.4 parts by weight of hexamethylenediamine, 51.76 parts of epsilon-aminocapronitrile, 2.5 parts of unreacted adiponitrile, and 5.9 parts of high boiling residue. The molecular yield of hexamethylenediamine was 40.3 per cent of the theoretical and of epsilon-aminocapronitrile 50.0 per cent of the theoretical, which corresponds to a recovery of 90.3 per cent of useful products.

The above experiment was repeated using a nickel-on-kieselguhr catalyst. There was obtained 2.3 parts of hexamethylenimine, 17.1 parts of hexamethylenediamine, 50.9 parts of epsilon-aminocapronitrile, and 27.2 parts of high boiling residue consisting of a viscous, tarry undistillable mass. The combined weight of useful products from the reaction amounted to only 67.6 per cent of the theoretical.

Example III

100 parts of adiponitrile was hydrogenated in the presence of 75 parts of anhydrous ammonia and 7.5 parts of a mild-acting cobalt-on-alumina catalyst. The reaction was carried out under 2000 to 3000 lbs./sq. in. hydrogen pressure at 120° C. and was allowed to proceed for 2.5 hours, during which time approximately 60 per cent of the theoretical amount of hydrogen was absorbed. On working up the product according to the procedure described in Example I, there were obtained hexamethylenimine, hexamethylenediamine, epsilon-aminocapronitrile, and high boiling residue in molecular yields of 3.0 per cent, 39.6 per cent, 45.5 per cent, and 11.0 per cent, respectively. The combined yield of hexamethylenediamine and epsilon-aminocapronitrile corresponded to 85.1 per cent of the theoretical, based on the amount of adiponitrile employed as starting material.

Example IV

101 parts of sebaconitrile was mixed with 75 parts of anhydrous ammonia and 10 parts of an alloy-skeleton iron-cobalt catalyst containing 10 per cent of cobalt. The mixture was charged into a high pressure reaction vessel and hydrogenated under 1500 to 2500 lbs. per sq. in. hydrogen pressure at 120° C. The reaction was continued for about 50 minutes, during which time 50 per cent of the theoretical amount of hydrogen was taken up. The product was removed from the reaction vessel, filtered to separate the catalyst, the catalyst washed thoroughly with methanol, and the combined filtrate and methanol washings evaporated to remove the solvent. The residual product was then carefully worked up in a precision vacuum still to

obtain 37 parts of decamethylenediamine, B. P. 133° to 134° C./6 mm., 24 parts of 10-aminocapronitrile, B. P. 154° to 156° C./6 mm., 28 parts of unchanged sebaconitrile, B. P. 107° C./6 mm., and 11 parts of high boiling residue. These amounts correspond to molecular yields of 36 per cent of decamethylenediamine, 24 per cent of 10-aminocapronitrile, 29 per cent of unreacted sebaconitrile, and 12 per cent of residue. The total amount of useful products, including sebaconitrile, suitable for recycling in the process was 88 per cent of theory.

Although in the foregoing examples certain definite conditions of temperature, pressure, catalyst, ammonia concentration, and the like have been referred to, it is to be understood that these values may be varied somewhat within the scope of the invention without departing from the spirit thereof. Broadly speaking, the specific conditions to be employed in the partial hydrogenation of a particular aliphatic dinitrile will be governed to a large extent by such interdependent factors as the physical and chemical properties of the dinitrile, by the relative distribution of products desired, and by the type of cobalt catalyst employed.

In the partial hydrogenation of aliphatic dinitriles coming within the scope of this invention, the success of the process depends not only on the specific, highly selective properties of the catalyst but also on the proper exercise of control over the rate and extent of hydrogen absorption. For example, if an insufficient amount of hydrogen is taken up, substantial amounts of unreacted dinitrile will remain, and if the mixture is over-hydrogenated the yield of desired omega-aminonitrile will be correspondingly low. Broadly speaking, the absorption of hydrogen in amounts corresponding to about 40 to 70 per cent of the quantity theoretically required for the complete conversion of the nitrile groups to amino groups will be found to give satisfactory results from the point of view of both total yield and conversion to omega-aminonitrile.

In general, the process of the invention may be operated at temperatures above about 25° C. and hydrogen pressures exceeding about 10 atmospheres and limited only by the mechanical strength of the equipment used in the hydrogenation. As a rule temperatures in excess of 200° C. are not employed in the practice of this invention. It is preferred to use temperatures between 100° and 140° C. and hydrogen pressures within the range of 30 to 300 atmospheres. The selection of a particular set of conditions within these ranges will, as mentioned above, be determined to a considerable extent by physical and chemical properties of the nitrile, and by the activity of the catalyst. It is particularly important that the absorption of hydrogen should proceed at a readily measurable rate so that the extent of hydrogenation can be controlled within the prescribed limits. Another important consideration that must be taken into account is to maintain an adequate concentration of anhydrous ammonia in the reaction mixture, preferably in excess of 20 parts per 100 parts of nitrile, in order to minimize side reactions involving the formation of polymeric secondary amines or other products. In this connection it should be pointed out that the total pressure of the reaction mixture should at all times exceed the partial pressure of ammonia vapor.

In the practice of this invention mild-acting cobalt hydrogenation catalysts are employed in

the partial hydrogenation of aliphatic dinitriles. Generally speaking, suitable cobalt catalysts may be prepared by conventional methods described in the prior art. Alloy-skeleton catalysts prepared by caustic activation of iron-cobalt-aluminum alloys are particularly desirable if high conversions to the aliphatic aminonitriles are desired, and, as shown in the above examples, an alloy-skeleton iron-cobalt catalyst containing

5 5 to 10 per cent by weight of cobalt and 95 to 90 per cent by weight of iron may be employed to convert adiponitrile to epsilon-aminocapronitrile in yields ranging up to 68 per cent of theoretical. Another type of cobalt catalyst suitable for the partial hydrogenation of aliphatic dinitriles may be prepared by reducing anhydrous cobalt salts or oxide with solutions of sodium naphthalene in the dimethyl ether of ethylene glycol, as described in U. S. Patent No. 2,177,412, issued October 24, 1939. Other types of cobalt catalysts can be prepared by precipitation of cobalt carbonate on suitable porous supports such as pumice, kieselguhr, silica gel, and the like, and subsequently reducing in a stream of hydrogen at temperatures between 400° C. and 450° C. This invention is not limited to the use of cobalt-containing catalysts referred to above since active cobalt-containing catalysts prepared by any other method known to the art may be employed successfully in the practice of this invention.

Generally speaking, the process of this invention is applicable to aliphatic dinitriles containing at least four carbon atoms in contiguous relation between the nitrile groups. As mentioned in the examples, adiponitrile and sebaconitrile are conveniently hydrogenated to the corresponding omega-aminonitriles. Among other aliphatic dinitriles coming within the scope of this invention are beta-methyl adiponitrile, pimelonitrile, suberonitrile, azelaonitrile, 1,9-dicyananonane, 1,10-dicyanodecane, 1,16-dicyanohexadecane, 2-hexyl sebaconitrile, and the like. The process of this invention is not applicable to dinitriles containing less than four carbon atoms in contiguous relation between the nitrile groups owing to the tendency of such compounds to undergo cyclization to produce polymethylenamines. This behavior is one of the well known properties of dinitriles such as glutaronitrile and succinonitrile, which react smoothly to produce piperidine and pyrrolidine respectively. Other short-chain dinitriles may react intermolecularly to produce cyclic products containing two secondary amino groups.

55 The process of this invention offers many advantages for the production of omega-aminonitriles. Mild-acting cobalt-containing catalysts are outstanding in their selectivity as regards the partial reduction step and also show little tendency to promote undesirable side reactions which are encountered with other catalysts, particularly nickel. It will be noted in the examples that with cobalt catalysts 85 to 90 per cent of the starting material is converted to useful products whereas with nickel much of the dinitrile is converted to tarry by-products, which not only leads to reduced yields of useful materials but causes difficulties in the separation of the desired products, considerations which are of exceeding importance in large scale commercial operation. The omega-aminonitriles per se are valuable chemical intermediates for the production of resins, other high molecular weight polymeric products, and modifying agents for resins, surface-active chemicals, and the like. The omega-

aminonitriles may also be conveniently hydrolyzed to the corresponding amino acids. Aliphatic diamines which are obtained in the practice of this invention are valuable intermediates for the manufacture of linear superpolymers.

Having described in detail the preferred embodiments of the invention, it is to be understood that the invention is not limited except as defined by the following claims.

I claim:

1. A process for the production of omega-amino-aliphatic nitriles which comprises bringing an aliphatic dinitrile having at least 4 carbon atoms in contiguous relationship between the nitrile groups in the liquid phase and in the presence of ammonia into contact with a mild-acting, cobalt-containing, hydrogenation catalyst at a temperature within the range of 100° to 140° C. and under a hydrogen pressure between 30 and 300 atmospheres and discontinuing the hydrogenation when an amount of hydrogen equivalent to from 40% to 70% of the theoretical amount necessary for the conversion of the dinitrile to the diamine has been absorbed.

2. A process for the production of omega-amino-aliphatic nitriles which comprises bringing an aliphatic dinitrile having at least 4 carbon atoms in contiguous relationship between the nitrile groups in the liquid phase and in the presence of ammonia into contact with a mild-acting, alloy-skeleton, iron-cobalt, hydrogenation catalyst at a temperature above 25° C. and at a hydrogen pressure in excess of 10° atmospheres, and discontinuing the hydrogenation when an amount of hydrogen equivalent to from 40% to 70% of the theoretical amount necessary for the conversion of the dinitrile to the diamine has been absorbed.

3. A process for the production of omega-amino-aliphatic nitriles which comprises bringing an aliphatic dinitrile having at least 4 carbon atoms in contiguous relationship between the nitrile groups in the liquid phase and in the presence of ammonia into contact with a mild-acting, alloy-skeleton, iron-cobalt, hydrogenation catalyst containing 5% to 10% by weight of cobalt and 95% to 90% by weight of iron at a temperature above 25° C. and at a hydrogen pressure in excess of 10 atmospheres, and discontinuing the hydrogenation when an amount of hydrogen equivalent to from 40% to 70% of the theoretical amount necessary for the conversion of the dinitrile to the diamine has been absorbed.

4. A process for the production of omega-amino-aliphatic nitriles which comprises bringing an aliphatic dinitrile having at least 4 carbon atoms in contiguous relationship between the nitrile groups in the liquid phase and in the presence of anhydrous ammonia in an amount of approximately 20 parts ammonia to 100 parts nitrile into contact with a mild-acting, cobalt-containing, hydrogenation catalyst at a temperature above 25° C. and at a hydrogen pressure in excess of 10 atmospheres, and discontinuing the hydrogenation when an amount of hydrogen equivalent to from 40% to 70% of the theoretical amount necessary for the conversion of the dinitrile to the diamine has been absorbed.

5. The process in accordance with claim 1 characterized in that the aliphatic dinitrile is adiponitrile.

6. The process in accordance with claim 1 characterized in that the aliphatic dinitrile is sebaconitrile.

GEORGE WAYNE RIGBY.