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PRODUCTION OF PRIMARY AMINES

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This invention relates to the production of aliphatic amines through the hydrogenation of aliphatic nitriles. This procedure as practiced conventionally in the art causes the formation of primary and secondary amines and other complex bodies. The secondary amines are of much less commercial value than the primary amines and the principal objective of the present invention has been to provide a process in which the yield of primary amines is much higher than that provided by the methods heretofore available.

The problem of obtaining satisfactory yields of primary amines is a difficult one and a variety of expedients has been proposed to improve the primary amine output and prevent secondary amine formation. Such measures as the use of special catalysts, the use of high pressures, hydrogenation in the presence of moisture and alkali and other substances have been proposed. The ordinary hydrogenation of nitriles produces about equal quantities of primary and secondary amines. By the special measures which have been proposed production of the primary product has been said to be increased to as high as 60% or 70%, but even this improvement is far from being fully satisfactory.

I have discovered, briefly, that the production of primary amines can be markedly increased and that yields closely approaching theoretical results may be obtained easily and conveniently by conducting hydrogenation of nitriles in the presence, paradoxically, of a substantial quantity of secondary amine or amines. In the past the effort usually has been made to keep the amount of secondary amines present in the reaction mix as low as possible at all stages of the reaction. According to the present invention, however, secondary amines are purposely caused to be present in the reaction zone. It is believed that by this presence the tendency of secondary amines to be formed from the nitriles being hydrogenated is either reduced or satisfied; as a result, at any rate, the formation of primary amines takes place without difficulty. Subsequently the secondary amines which were present to foster the reaction are separated from the primary reaction products and may be used to like advantage in the hydrogenation of another batch of nitriles.

Aside from the presence of the secondary amines which purposely is established and maintained in the zone of reaction the process of the present invention may follow conventional procedures and may be conducted either in the liquid or the vapor phase. The nitriles are subjected to hydrogenation at elevated temperature and pressure in the usual manner until the reaction

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is completed as indicated by hydrogen no longer being absorbed. Thereafter the primary amines produced are separated from the secondary amines which were employed to foster the reaction by any suitable separation method as, for example, by vacuum distillation. Nickel or platinum catalysts are used to facilitate hydrogenation and the temperature at which the operation is carried out preferably is about approximately 200° C. although the temperature is not of critical importance and the reaction preferably is conducted in the presence of ammonia. According to this process yields may be obtained as high as 100% of theoretical, and yields of 85% to 90% may be expected as a day in, day out, matter as distinguished from the 60% to 70% production which heretofore has been described as excellent results.

In the preferred practice of the present invention a batch of nitriles is hydrogenated in a conventional way to obtain a mixture of primary and secondary amines and the secondary amines in this batch are used to foster the production of primary amines in the hydrogenation of another batch of nitriles. The secondary amines obtained in this manner may be used over and over again at substantially no cost. The mixture of primary and secondary amines, as produced by hydrogenation of nitriles in a conventional way, may be used for the purpose of improving the yield of primary amines by adding the mixture directly to a later batch of nitriles to be hydrogenated, or secondary amines present in the mixture may be separated from the primary amines by distillation and then used in the same manner. However, in the alternative, secondary amines obtained from other sources may be utilized.

It has been noticed in the course of the investigation which led to this invention that at certain times, or under certain conditions, the yield of primary amines has apparently been greater than could have formed from the nitriles employed. A possible explanation is that under the conditions, part of the primary amines were formed from the secondary amines.

So long as a definite relatively appreciable quantity of secondary amines is present the precise amount employed is not critical, noting, however, that excessive quantities are not desirable because they increase the cost of separation of primary amines without proportionately increasing the yield of it. Usually from 50% to 200% by weight of secondary amines for each part of nitrile to be hydrogenated gives suitable results.

From the foregoing disclosure of the principles of the present invention and from the following

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disclosure of typical examples of the process those skilled in the art readily will comprehend the modifications to which the improvement is susceptible.

Example I

200 parts of nitriles derived from commercial stearic acid and 1 part of Raney nickel catalyst were placed in an autoclave and subjected to hydrogenation using a partial hydrogen pressure of 300# and a partial ammonia pressure of 100#. The hydrogenation was conducted at a temperature of approximately 210° and the autoclave was of the rocking variety for agitation.

Absorption of hydrogen by the nitrile had substantially stopped after about fifteen minutes. The primary amines were recovered by vacuum distillation of the product to a temperature of approximately 270° C. at 50 mm. pressure. The distillate, consisting of primary amines, amounted to only approximately 64% of the amount theoretically available from the nitrile used.

The residue of the distillation consisted essentially of secondary amines and, in accordance with the present invention, 200 parts of nitriles were now hydrogenated in the presence of 100 parts of this secondary amine residue, using 1 part of Raney nickel catalyst. This hydrogenation was conducted in the manner just described. Hydrogen absorption practically stopped after thirty minutes and the primary amines were separated by distillation as described. In this case, however, primary amines were produced amounting to 84% of the quantity theoretically obtainable from the nitriles used.

Example II

Using a ratio of 2 parts residue consisting essentially of secondary amines to one part of nitriles in the process described in Example I a yield was obtained representing 98% conversion of the nitriles to primary amines.

Example III

As distinguished from the hydrogenation of the nitrile of commercial stearic acid, which is actually a mixture of high molecular weight fatty acids, the following example shows the hydrogenation of pelargonyl nitrile, the nitrile of a comparatively low molecular weight fatty acid:

200 parts of pelargonyl nitrile and 2 parts of Raney nickel catalyst were placed in a rocking autoclave and subjected to partial hydrogenation pressure of 350# and a partial ammonia pressure of 50# at 210° C. Hydrogen absorption had substantially stopped after about forty-five minutes. Primary amine obtained by distillation of the product to 250° C. at atmospheric pressure amounted to 49% of the quantity of primary amines theoretically available. However, 200 parts of the residue from this distillation, consisting essentially of secondary pelargonyl amine, was added to 100 parts of pelargonyl nitrile and the latter hydrogenated in the manner described in the presence of approximately 1 part of Raney nickel catalyst. Hydrogen absorption stopped after approximately 75 minutes and the amount of primary pelargonyl amine obtained by distillation of the hydrogenated nitrile amounted to approximately 74% of the amount theoretically available based on the amount of nitrile used.

Example IV

Nitriles of the higher molecular weight fatty acids obtained from hydrogenated fish oil, that is, fatty acids of from 20 to 22 carbon atoms in

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chain length, were hydrogenated as described in Example I. Hydrogenation was continued until hydrogen absorption stopped, a period of approximately forty-five minutes. The product resulting from the hydrogenation was subjected to vacuum distillation to a temperature of 300° C. at 35 mm. pressure, and primary amines were obtained amounting to approximately 69.1% of the quantity of primary amines theoretically available.

100 parts of the nitriles of higher molecular weight fatty acids of hydrogenated fish oil were hydrogenated in the presence of approximately 130 parts of the residue resulting from the foregoing distillation, this residue consisting essentially of secondary hydrogenated fish oil fatty acid amines. The hydrogenation was conducted in the presence of approximately one-half part of Raney nickel catalyst. In this operation the absorption of hydrogen had substantially stopped after sixty minutes and the primary amines produced were recovered by vacuum distillation of the hydrogenated product to a temperature of approximately 300° C. at 35 mm. pressure. The yield amounted to over 100% of the amount theoretically available from the quantity of nitriles used. The difference, as previously explained, is attributed to the conversion of some secondary amine into primary amine.

The foregoing examples illustrate the practice of the present invention on representative high and low molecular weight fatty acid nitriles, representative nitriles other than those disclosed being the nitriles of palmitic and lauric acid and like fatty acids which may be obtained from commercial fats.

In vapor phase reactions as distinguished from the liquid phase reactions disclosed in the examples the secondary amine selected is one which is volatile at the reaction temperature. Once the secondary amine has been produced, as in the methods disclosed in the examples, or is available from other sources, it may be used repeatedly without substantial loss, decomposition or conversion. It is usually preferable to use a secondary amine of a fatty acid corresponding to the fatty acid from which the nitrile was derived in order to avoid contaminations. However, this is not essential and secondary amines of fatty acids which are different from the fatty acids from which the nitriles were derived may be employed, for example, secondary lauric amine may be used to increase the yield of primary amine from a stearic acid nitrile or the like.

Having described my invention, I claim:

1. In the process of manufacturing primary amines by catalytically hydrogenating nitriles in the presence of ammonia and distilling said primary amines from the secondary amines formed in the hydrogenation, the step of adding the secondary amine residues remaining after distilling the primary amines to each succeeding batch of nitrile to be hydrogenated.

2. The method of converting long chain aliphatic nitriles into corresponding primary amines, which comprises admixing with said nitriles a quantity of corresponding secondary amine sufficient substantially to inhibit further formation of secondary amines, then catalytically hydrogenating said admixture in the presence of ammonia, recovering said primary amines by distilling them from the secondary amines, and remixing said secondary amines with a new batch of nitriles to be hydrogenated.

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