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PROCESS FOR PREPARING NITRILES

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It has been well-known for a long time (B 17 (1884), 73, 2332, 2337, 2343; B 18 (1885), 138, 1002), that the decomposition of formylamines by heat forms nitriles, but the yield of nitriles in said decomposition by heat did not surpass 20% of the formylamines employed.

Later on it was found (Mailhe C.r. 176, 689 (1923), that on passing formaniline vapour over Al_2O_3 at 400° C., a small amount of benzonitrile is formed in addition to carbon monoxide and aniline.

These observations were taken up in German patent specification No. 482,943 (1929), in which it is shown that by passing formic salts of primary amines or formylamides over porous contact substances, the respective nitriles are generally obtained.

The reaction that takes place is probably as follows: at first the isonitriles are formed from the formylamines, and from the isonitriles there are formed the nitriles by transposition at very high temperature. This may be represented by the following reaction scheme:

$$\underset{\displaystyle \mathrm{H}}{\mathrm{RN}}.\mathrm{COH} \longrightarrow \mathrm{RNC} + \mathrm{H_2O} \longrightarrow \mathrm{RCN}$$

Benzonitrile is obtained by a similar reaction, here too through the intermediate formation of isonitrile by heating phenyl isosulfocyanate with powdery copper (B 6, 212 (1873)). German patent specification No. 259,364 describes, and is based on, this observation.

While the second mentioned process has but slight industrial importance, owing to the comparatively high cost of raw materials, the first mentioned process might achieve fundamental importance, since formylamines can be obtained in a comparatively easy way from amines and carbon monoxide, the cost of which is not high.

According to patent specification No. 482,943, as described in the examples, vapours of formic salts of amines, of formylamines or of mixtures of amines with esters of formic acid are passed over contact substances; now, it is hardly possible to prepare vapours of formic salts of amines as such and, therefore, to convey them through pipes; at any rate, in the examples of specification 482,943 it is not even said in what manner such vapours are produced and transported. It is assumed that probably they reach the catalyst in a liquid state and evaporate when touching the contact mass. It is evident that when operating in this way or in a similar manner, it is not possible to avoid decompositions. Consequently the process according to said specification gives low yields in the majority of cases. Also the examples in said specification may serve as a basis for computing the yields only in some cases, since no distinction is made between conversion after one passage and total yield.

In addition to the fact that the yields are comparatively low, operation in accordance with the cited patent specification causes a quick separation of resinous products, so that after even a few hours the contacts are useless.

Now it has been found that these drawbacks can be avoided and that it is possible to increase yields and conversions to a relevant extent, by passing the vapours of the formyl compounds over the catalyst only in a highly diluted condition. This can be obtained by passing through the molten formyl compounds heated to elevated temperature, a stream of an inert gas which becomes saturated with the vapours of said formyl compounds by evaporation of the latter, and carries said compounds so diluted, to rearrangement through the catalyst. As an inert gas it is possible, to use for instance, nitrogen, carbon monoxide or hydrogen. A still better result has been attained by operating under vacuum instead of with an inert gas. The formyl compounds are evaporated by the use of vacuum, e.g. of 20–40 mm. Hg, and the vapours so diluted are made to react directly through the catalyst, without using further diluents. In both cases, the evaporating temperatures of the formyl derivatives should be as high as possible to obtain a velocity of evaporation high enough to allow transportation of vapours but, on the other hand, said temperatures should remain below the decomposition point of the corresponding formyl amines, otherwise the yields will decrease. Generally speaking, the most convenient temperatures are those corresponding to the boiling point of the formyl derivative at a vacuum of 20–30 mm.

The improvement attained in the stability and permanence of the catalyst and above all in yield and in conversion, especially if vacuum is used, is so unexpectedly marked that it cannot be explained in any obvious manner. It is true that formyl amides are often sensitive to high temperatures and decompose easily with the separation of CO. This may explain why it is possible to increase the yields if evaporation is carried out with greater care. However, the substantial improvements afforded by the new process are not likely to be due only to this factor.

As already said above, it is assumed that an isonitrile is obtained as an intermediate product in the formation of nitriles, which isonitrile transforms into a nitrile at the elevated temperature of the catalyst chamber. Better to explain the unexpected improvement due to the new process, it may be suggested, among other things, that when diluted vapours are employed, owing to the shorter time of contact with the catalyst, the intermediate isonitriles do not resinify so easily any more. By this new process, yields of 98–100% are obtained, calculated on the amine employed, and conversions up to 70–80% after one passage only.

A further and essential advantage of this novel process is that the catalyst remains active for some weeks; conversions diminish slightly only after much prolonged use, but even then the yields are not lowered. When after some weeks of operation the conversion with one passage has at last diminished by 5 to 8%, it suffices merely to treat the catalyst with air to render it quite effective again.

The present process can be employed with particular success for the preparation of those nitriles which carry on their nucleus a further hydrocarbon group. For instance, it serves to prepare p-tolunitrile from p-toluidine

(p-tolunitrile being a starting material for preparing terephthalic acid and synthetic resins); and cyancumene (which too is a starting material for synthetic resins) from p-aminocumene.

Broadly speaking, the operational steps of the new process are as follows:

The formyl amine to be reacted is melted and heated to boiling under a vacuum of 20 mm. of Hg in a vessel that can be heated up to 200–250° C. in an oil bath. The vessel is provided with a discharge pipe and a thermometer. The vapours produced pass through the discharge tube into a pipe heated to about 500° C., which is packed either with silica gel, or with carbon (charcoal), aluminum oxide, boron phosphate or another known catalyst; the vapours pass through this tube, whereafter the products of reaction are condensed with the usual means.

If the operation is carried out without using any vacuum, the vessel is equipped with a pipe for the introduction of a gas, which extends to the bottom of the vessel and is connected with a source of nitrogen, carbon monoxide or hydrogen. The pipe may be provided with devices for the better distribution of the gas stream within the liquid. Pre-heating of the gas is not required, but may be provided. The gases saturated with the vapours of formylamine pass through the apparatus in the manner hereinbefore described in setting forth the first embodiment of the process.

For the treatment of the reaction products, the usual method may be employed. Usually the reaction product is composed of free amine and nitrile, but it may contain a very small portion of unreacted formyl derivative. It may be treated e.g. with diluted mineral acids; the amine dissolves and the nitrile separates as an insoluble layer; it can be separated and finally purified by distillation.

The aqueous solution containing the amine is rendered alkaline, and this causes the separation of said amine, which can be recovered.

The formyl derivatives that may be present in the product if the starting compounds contain a side chain, generally dissolve in the nitrile from which they can be separated by distillation. In the case of aniline, the greater part of the formyl derivative is found in the aniline layer.

In lieu of a diluted mineral acid, formic acid may be used and so, following conventional methods, the formyl derivative may be prepared directly from the formic salt of the amine.

The following examples better illustrate the process:

Example 1

The apparatus consists of an iron vessel of 3 litres capacity placed in an oil bath adapted to be heated and on which there is mounted a vacuum-proof cover or lid. The lid carries a joint with a cock for the introduction of the starting material, a joint with a thermometer and a joint for the connection of the catalyst tube. The catalyst tube is a simple iron tube with electric heating, having an internal diameter of 30 mm., on the bottom of which there is applied a coarse mesh sieve, upon which the catalyst is placed in a layer of about 100 cm. A silica gel of 4–5 mm. grain size is used as a catalyst. The temperature in the catalyst tube is kept at 490–500° C. by means of a thermometer provided with an adjusting device. At the upper end of the catalyst pipe there is applied a downward condenser ending in a receiving vessel connected with the vacuum pump.

To carry out the experiment, 1730 g. of molten formanilide are introduced into the vessel, the vacuum pump is started and the oil bath is heated to 245–255° C. with a vacuum of 20 mm. and an internal temperature of about 185° C. there are evaporated about 200 g./hour of formanilide. The vapours pass through the catalyst chamber kept at 500° C. and are thereafter condensed in the cooler and collected in the receiving vessel. When all the formanilide is evaporated, the experiment is broken off and the distillate is worked up. It is stirred with diluted hydrochloric acid in such an amount as to render the solution acid, with a pH equal to 1, and the layers formed are separated. The aqueous portion is stirred again with ether and the ether solution is joined to the oil, previously separated. After evaporating the ether and distilling the residue, 810 g. of benzonitrile and 45 g. of unreacted formanilide are obtained, which corresponds to a 58.4% conversion of formanilide into benzonitrile. The aqueous portion is made alkaline by means of sodium hydroxide and the aniline separated is distilled; 482 g. are obtained. The total yield, taking into account the aniline recovered, is 99%, calculated on the aniline employed.

When working without vacuum according to German Patent 482,943 (Example 3), from aniline and ethyl ester of formic acid there is obtained a benzonitrile yield of only 25% of the theoretical amount.

Example 2

332 g. of formyl cumidine, obtained by formylation of a crude mixture of (about 15%) o- and (about 85%) p-cumidine (isopropylaniline), are evaporated under a vacuum of 30 mm. Hg and a temperature of 220–230° C.; the vapours are passed over the catalyst heated to 500° C., as described in Example 1, and the condensate is treated as before: 166 g. of isopropylbenzonitrile and 77 g. of cumidine are obtained. In this case the conversion into isopropylbenzonitrile is 56.1% and the amine recovered is 28.1%, both figures calculated on isopropylformamide. The yield is only 85%, owing to the impurity of the starting material employed. Hence the ratio between the amounts of amine and of nitrile, is almost exactly 1:2. Comparative experiments carried out without using vacuum, gave about the same yields of 85%, but the average ratio between amine and nitrile amounts was only 1:1.2.

Example 3

965 g. of p-methyl formanilide are evaporated as in Example 1 with a vacuum of 20 mm. Hg, an internal temperature of 185–190° C. and at a speed of about 200 g./hour and the vapours are passed over the catalyst heated to 500° C. From the condensate, 240 g. of p-toluidine and 564 g. of p-tolunitrile (p-methylbenzonitrile) are obtained.

Taking into account the amount of substance recovered, the yield is 98.3% of theory. The conversion of formyl toluidine into tolunitrile is 67.5%. Comparative experiments without the application of a vacuum give a yield of 89% of the theoretical amount and the conversion of p-formyltoluidine into p-tolunitrile is 35% of the theoretical amount.

Example 4

300 g. of p-methyl formanilide are heated at atmospheric pressure to 210° C. and a nitrogen stream is passed through the molten mass. The formyl amide vapours entrained by the nitrogen, pass over the catalyst heated to 500° C. There are obtained 280 g. of a condensate, from which 165 g. of p-methyl benzonitrile are obtained. Moreover, 85 g. of p-toluidine are recovered. Consequently this process yields 98.9% of the theoretical amount of p-methyl benzonitrile. Conversion is 63.5%.

We claim:

1. The method of preparing monocarbocyclic aryl nitriles of the formula RCN, where R is monocarbocyclic aryl, comprising passing vapors of a monocarbocyclic formyl amine of the formula RNHCOH, wherein R is monocarbocyclic aryl, over a dehydration catalyst under vacuum in the range of 20–40 mm. Hg at elevated temperatures.

2. The method as defined in claim 1 wherein the vapors

of the said formyl amine are produced by distilling under vacuum in the range of 20–40 mm. Hg to form vapors thereof prior to contact with the catalyst.

3. The method of preparing monocarbocyclic aryl nitriles of the formula RCN, where R is monocarbocyclic aryl, comprising melting a monocyclic formyl amine of the formula RNHCOH, wherein R is monocarbocyclic aryl, at atmospheric pressure, passing a stream of inert gas through the molten mass, and conducting vapors of the formyl amine in the inert gas over a dehydration catalyst.

4. The method of claim 3, wherein the inert gas is nitrogen.

5. The method of claim 3, wherein the inert gas is carbon monoxide.

6. The method of claim 3, wherein the inert gas is hydrogen.

References Cited in the file of this patent

FOREIGN PATENTS

482,943 Germany ---------- Sept. 25, 1929