

ALIEN PROPERTY CUSTODIAN

PRODUCTION OF ALICYCLIC ALCOHOLS

Willi Schmidt and Karl Seydel, Ludwigshafen-on-Rhine, and Hugo Kroeper, Heidelberg, Germany; vested in the Alien Property Custodian

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This invention relates to the production of alicyclic alcohols; and more particularly it concerns the production of such alcohols from cyclic nitrogenous compounds containing six-membered carboxylic rings and one nitrogen atom, the rings being free from substituents other than those containing exclusively carbon and hydrogen atoms.

Cyclohexanol and its homologues and analogues in general are extremely valuable as solvents and as starting materials in organic processes. Methods already are known for the production of such alcohols involving the hydrogenation of phenols in the presence of catalysts.

The present invention is based upon the discovery that alicyclic alcohols may be prepared in highly satisfactory yields in a simple manner from starting materials different from phenols. By heating a compound of the type described above, for example cyclohexylamine, methylcyclohexylamine, dicyclohexylamine, decahydronaphthylamine, or mixtures thereof with hydrogen and a hydroxyl-containing compound, such as water or an alcohol, in the presence of a hydrogenation catalyst, alicyclic alcohols are formed together with ammonia or ammonia substituted by the radicle of the hydroxyl-containing compound.

In its broadest scope the invention involves heating cyclohexylamine or its homologues or analogues or any compound capable of being converted into or capable of yielding cyclohexylamine or its homologues or analogues with hydrogen and a hydroxyl-containing compound in the presence of a hydrogenation catalyst.

As catalyst there may be used in particular the metals of the 8th group of the Periodic Table, in particular the non-noble metals, or copper metal or oxydic or sulfidic hydrogenation catalysts. The preparation and the composition of these catalysts has extensively been studied and described in connection with the catalytic hydrogenation of aniline to form cyclohexylamine, with the production of alcohols from fatty acids or with the conversion of carboxylic acids, ammonia and hydrogen into amines or with the production of amines from carboxylic acid nitriles. These catalysts may be employed either alone or applied to the conventional carrier substances, such as pumice stone, aluminium oxide, fused silica gel and the like. It will be understood that the above given explanation of the catalysts is merely given for purposes of illustration and that the specific catalyst is not an essential part of our invention but that numerous modifica-

tions of these catalysts may be made without departure from the spirit of our invention and that any other of the catalysts employed in hydrogenations of the type referred to above may be used.

The reaction according to our invention is preferably carried out under energetic conditions. The catalysts should be employed in a highly active state and the process is conducted preferably at temperatures ranging from 160 to 400°C, and in particular from 180° to 330°C. When working in the vapor phase, it is particularly suitable to work at temperatures below 250°C; the liquid phase process is preferably conducted at temperatures exceeding 220°C. A substantial excess of the hydroxyl-containing compound over that required to substitute a hydroxyl group for a nitrogenous group, e. g. the amino group, for example from 2 to 50 times, should be employed. Suitable hydroxyl-containing compounds are in particular water, and also low molecular aliphatic alcohols, such as methanol, ethyl, propyl or butyl alcohol and the like. It is self understood that higher alcohols may also be used but this does not involve economic advantages because too large a radicle attached to the hydroxyl group simply constitutes a diluent decreasing the yield per unit of time and reaction space and slowing up the process.

The reaction may be carried out in the liquid phase or in the gas phase. It is possible to employ inert solvents for the reactants or inert diluent gases when working in the gas phase. By working under superatmospheric pressure it is possible to maintain a high hydrogen concentration even when working with a considerable excess of the hydroxyl-containing compound. The pressure, when employed, may be within the range of from 10 to 250 atmospheres, but higher pressures, such as 300, 400, 500 or more may be employed.

The process may be conducted continuously for example by leading a vaporous mixture of cyclohexylamine, steam and hydrogen through a tube or a plurality of tubes charged with a hydrogenation catalyst. When working continuously in the liquid phase, the liquid mixture of cyclohexylamine and water or alcohol may be pressed through a vessel wherein the catalyst may be rigidly arranged, while at the same time leading hydrogen in the same direction in a cycle through the vessel. The liquid starting material may also be allowed to trickle over the catalyst while leading in hydrogen in counter-current together with

a vaporized hydroxyl-containing compound of the kind defined above.

The actual temperature to be used depends on the activity of the catalyst and on the time of contact between the reaction mixture and the catalyst. In general, the time of contact should be long enough to ensure that the starting material introduced is at least partly subjected to cyclohexanol formation before leaving the catalyst. However, the temperature should not be so high and the time of contact should not be so long as to favor substantially the formation of aromatic or alicyclic hydrocarbons which may occur under too energetic conditions.

A preferred embodiment of our invention consists in using as starting materials nitrogenous aromatic compounds which are capable of being converted under reaction conditions into cyclohexylamine or its homologues and analogues as defined above. Suitable compounds of this type are, for example, aniline, naphthylamine, diphenylamine or their alkyl substitution products, e. g. toluidines or phenylcyclohexylamine or even nitrobenzene, nitrosobenzene, phenylhydroxylamine, the nitrogenous group of which is easily converted into an amino group during or before the hydrogenation of the benzene nucleus.

Generally speaking, the reaction conditions for converting one of the aromatic nitrogenous compounds of the kind referred to above into alicyclic alcohols are similar to those used in the production of alicyclic alcohols from alicyclic amines. A substantial excess of the hydroxyl-containing substance should be employed. In selecting the hydrogenation catalyst care should be taken that the benzene nuclei are hydrogenated. Metals of the 8th group of the Periodic Table are particularly satisfactory in this respect. The reaction conditions should be chosen accordingly; in particular, the reaction is preferably carried out under increased pressure and at temperatures exceeding 250° C, if nitrohydrocarbons are the starting materials.

The following Examples serve to illustrate various modifications of our invention. It is, however, not restricted to these Examples. The parts are by weight unless otherwise stated.

Example 1

100 parts of nickel carbonate are intimately mixed with 4 parts of chromic acid anhydride and the whole then reduced in a stream of hydrogen.

10 parts of cyclohexylamine, 10 parts of water and 1 part of the catalyst are charged into a stirring autoclave and heated at 300°C with hydrogen under a pressure of 250 atmospheres for some hours. The reaction mass is allowed to cool, filtered off from the catalyst and admixed with sulphuric acid in order to eliminate the basic compounds. The cyclohexanol is then purified by distillation. 5 parts of cyclohexanol are thus obtained corresponding to a yield of 90 per cent calculated on the amount of cyclohexylamine converted.

When starting from 10 parts of dicyclohexylamine or of a mixture of equal amounts of cyclohexylamine and dicyclohexylamine, cyclohexanol is formed under otherwise identical conditions in a 93 per cent yield. Good yields are also obtained when lowering the reaction temperature to 250°C, the time of the reaction being somewhat longer.

Example 2

A mixture of 10 parts of aniline, 30 parts of methanol and 1 part of a copper catalyst applied to silica gel (copper content 20 per cent; chromic oxide content 0.9 per cent) are filled into a stirring autoclave. Hydrogen is then pressed in at room temperature under a pressure of 30 atmospheres. The whole is then heated to 300°C, whereby the pressure reaches 276 atmospheres. The reaction mixture is allowed to cool and the pressure is released. A mixture of hydrogen and methylamine escapes. The reaction mixture is filtered off and worked up in the manner described in Example 1. Cyclohexanol is thus obtained in a yield of 82 per cent.

Example 3

100 parts of cobalt carbonate are intimately mixed with 4 parts of chromic acid anhydride and the whole is reduced in a stream of hydrogen.

10 parts of aniline, 10 parts of water and 1 part of the catalyst are heated in a stirring autoclave to 300°C, while simultaneously pressing in hydrogen under a pressure of 250 atmospheres. During the reaction the hydrogen pressure is partly released three times in order to remove as far as possible the ammonia formed. After hydrogen is no longer absorbed, the reaction mixture is allowed to cool and filtered off from the catalyst. The oily layer of the filtrate is subjected to an azeotropic distillation with benzene in order to remove water. The cyclohexanol remaining back is purified by fractional distillation. The aminic bodies mostly mono- and dicyclohexylamine, obtained as by-products are again used for the production of cyclohexanol. The yield is 6.5 parts of cyclohexanol.

Example 4

20 parts of nickel oxide, 6 parts of copper oxide and 1 part of chromic oxide are precipitated on 7.3 parts of pumice stone. The catalyst is then reduced.

Over this catalyst there is led per hour 90 times its volume of hydrogen admixed with 3.5 per cent per volume of vaporous aniline and 25 per cent per volume of steam. The mixture emerging from the catalyst is condensed. From the condensate the ammonia dissolved therein is removed by gently heating and from the hydrogen the ammonia is also removed.

The ammonia-free condensate is vaporized in a stream of ammonia-free hydrogen and led over a catalyst of the above described composition under the same conditions. This process is repeated twice. The condensate obtained by cooling the reaction mixture emerging from the fourth catalyst is practically free from amines. The aqueous part of the condensate is given back into the mixture to be led over the first catalyst. The yield of crude cyclohexanol is 102 parts for 100 parts of aniline.

Example 5

Over 100 liters of a nickel catalyst activated by chromium, zinc and barium applied to pumice stone (the catalyst contains per 100 parts of nickel 2 parts of chromium oxide, 1.5 parts of zinc oxide and 2 parts of barium oxide) there is led per hour at from 180 to 190°C a mixture of 8,000 liters of hydrogen, 1,500 grams of vaporized aniline and 6,000 grams of steam. The gas mixture emerging from the catalyst is suitably condensed whereby two condensates are obtained, the first consisting of crude cyclohexanol and the second

of water free from ammonia. The residual gas consisting of hydrogen and ammonia is freed from ammonia. The hydrogen is again mixed with vaporous aniline and steam and thus again used for the reaction.

The crude cyclohexanol which contains small amounts of cyclohexanone is led together with hydrogen under 200 atmospheres pressure in the same direction over a nickel catalyst as described in Example 4 contained in a vertically arranged tower. The product thus obtained is separated by a fractional distillation into cyclohexanol and into amines which are given back into the first stage of the process. The yield of cyclohexanol amounts to from 94 to 96 per cent of the theoretical yield.

Example 6

12.3 parts of nitrobenzene, 10 parts of water and 1 part of the catalyst described in Example 1 are treated at 300°C with hydrogen under a pressure of 250 atmospheres for 6 hours. The reaction product is filtered off from the catalyst and then subjected to a fractional distillation. Cyclohexanol is thus obtained in a yield of 94 per cent of the theoretical yield.

Example 7

15. parts of para-toluidine, 10 parts of water and 1 part of the catalyst described in Example 1 are heated in a stirring autoclave to from 260° to 280° C while simultaneously pressing in hydrogen under 250 atmospheres pressure. During the reaction the pressure is released twice to 150 atmospheres.

The reaction mixture is worked up in the manner described in Example 1, whereby para-methylcyclohexanol is obtained in a yield of 91 per cent.

Example 8

10 parts of decahydronaphthylamine, 10 parts of water and 1 part of the catalyst described in Example 1 are heated in a stirring autoclave to from 280° to 300° C while continuously maintaining a hydrogen pressure of 250 atmospheres. The pressure is released three times down to 100 atmospheres. Decahydronaphthol is thus obtained in a 90 per cent yield.

WILLI SCHMIDT.
KARL SEYDEL.
HUGO KROEPER.