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PRODUCTION OF ALIPHATIC DI-CARBOXYLIC ACIDS

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8 Claims. (Cl. 260—112)

This invention relates to the production of aliphatic di-carboxylic acids. When cyclo-hexanol, cyclo-hexanone or the like compounds are oxidized under usual conditions by means of nitric, chromic or other suitable acids, considerable amounts of decomposition products such as succinic acid, glutaric acid &c. are always formed besides adipic acid. This also applies, to an increased degree, to alkyl-substituted hydrogenated phenols.

Now I have found that the course of reaction is favored in two respects by the addition of an oxidative catalyst, for instance metallic oxides and the salts derived therefrom, such as mercuric oxid or mercuric sulfate, molybdenic oxid and, especially, vanadic oxid or ammonium vanadate. Such additions enable me to proceed with lower temperatures and with a considerably reduced quantity of oxidizing agents, and furthermore the decomposition is diminished to a minimum, whereby the yield of di-carboxylic acids (adipic acid &c.) primarily formed is considerably increased.

The same advantages appear when any desired hydroaromatic, especially alicyclic alcohols, such as tetrahydronaphthol or decahydronaphthol are subjected to oxidation.

My invention enables oxidation, for instance, at 50 to 60° C., whereas without the addition of a catalyst the oxidation does not take place at all, or only to a slight degree, at this temperature, and a temperature of 90 to 95° C is required for maintaining the reaction. Owing to the higher temperature an increased decomposition takes place being observable by greater quantities of carbon-dioxide formed and an increased consumption of nitric acid.

Of course, I may employ as starting materials the primary oxidation products of the cyclic alcohols, i. e. the respective ketones, for instance tetrahydro-naphthalene-ketone, or hydrindone &c. instead of the cyclic alcohols themselves.

Examples

1. 200 grams of cyclohexanol are slowly and dropwise added to 840 grams of nitric acid of 50% HNO₃ containing 0.4 gram of ammonium vanadate, the initial temperature of the acid being 50° C. The reacting mass is kept at 50–60° C. by intense cooling. 220–225 grams of adipic acid were obtained; from the mother liquor 50 grams of a mixture of acids were separated, mainly consisting of succinic and glutaric acid.

2. 4.2 kilograms of a 50% nitric acid are heated to 50–60° C., and after addition of 2 grams of

ammonium vanadate or 5 grams of molybdenic oxid 1 kilogram of methyl-cyclohexanol is slowly run in, care being taken that the reaction temperature may not exceed 65° C. After completing the oxidation the acid solution is evaporated to about one fourth of its total volume and cooled down. The crude methyl-adipic acid separates forming fine crystals; by recrystallizing the acid from a little hot water it is obtained with a yield of 950 to 1000 grams. A further amount of 250–300 grams may be obtained from the mother liquor, after separating the catalyst, by complete evaporation.

When operating without a catalyst the total yield of acids obtained in several steps amounted to 85–105% of the hydrophenol employed, whereas with the catalyst the least yield was 120%, only 62% of the nitric acid required when operating without a catalyst being needed.

3. 228 grams of p-methyl-cyclohexanol are oxidized with 1000 grams of nitric acid of 60% HNO₃ to which 200 grams of water and 2.5 grams of mercuric sulfate have been added. The oxidation begins at 50° C. which temperature is maintained during the introduction of the methyl-cyclohexanol. 223 grams of methyl-adipic acid and 50 grams of low-molecular acids were obtained.

4. In the same manner as described in the foregoing example, 245 grams of adipic acid are obtained from 200 grams of cyclohexanol. The product, after recrystallization from water, has a definite melting point of 151–152° C. and a pure white color.

In the same manner as described in Example 2, α-β-dimethyl-adipic acid is obtained by oxidizing 1,3,5-hexahydroxylenol.

5. 800 grams of decahydronaphthol are gradually introduced into 3.5 kilograms of a 60% nitric acid, heated to about 50° C., to which 1.5 grams of ammonium vanadate were previously added. The treatment of the oxidation products yields substantially a mixture of cis- and trans-hexahydro-o-phenylene-diacetic acid melting at 164° C and 151° C. respectively, and hexahydro-o-carboxylic phenyl propionic acid which products may be separated in any suitable way.

I claim:—

1. The process of producing aliphatic dicarboxylic acids comprising the oxidation of material of the group consisting of hydro-aromatic and alicyclic alcohols and their primary oxidation products by an oxidizing acid in the presence of an oxidation catalyst derived from a polyvalent metal.

2. The process of producing aliphatic dicarboxylic acids comprising the oxidation of material of the group consisting of hydro-aromatic and alicyclic alcohols and their primary oxidation products by an oxidizing acid in the presence of an oxidation catalyst derived from a polyvalent metal at a temperature approximating 50 to 60° C. 80
3. The process of producing aliphatic dicarboxylic acids comprising the oxidation of material of the group consisting of hydro-aromatic and alicyclic alcohols and their primary oxidation products by an acid of the group consisting of concentrated nitric acid and chromic acid in the presence of a catalyst of a group consisting of mercuric oxide, mercuric sulfate, molybdenic oxide, vanadic oxide and ammonium vanadate. 85
4. The process of producing aliphatic dicarboxylic acids comprising the oxidation of material of the group consisting of hydro-aromatic and alicyclic alcohols and their primary oxidation products by an oxidizing acid in the presence of a catalyst consisting of a vanadium-oxygen compound. 90
5. The process of producing aliphatic dicarboxylic acids comprising the oxidation by a strong oxidizing acid of an alicyclic alcohol in the presence of an oxidation catalyst comprising a polyvalent metal oxide capable of forming an acid. 95
6. The process of producing adipic acid comprising oxidizing a material of the group consisting of cyclohexanol and cyclo-hexanone by an oxidizing acid in the presence of an oxidation catalyst comprising a polyvalent metal oxide capable of forming an acid. 100
7. The process of producing adipic acid comprising oxidizing a material of the group consisting of cyclohexanol and cyclo-hexanone by an oxidizing acid in the presence of an oxidation catalyst comprising a polyvalent metal oxide capable of forming an acid at a temperature approximating 50 to 60° C. 105
8. The process of producing aliphatic dicarboxylic acids comprising the oxidation of hydro-aromatic alcohols containing six or more carbon atoms by strong oxidizing acids in the presence of an oxidation catalyst comprising a polyvalent metal oxide capable of forming an acid. 110
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