

ALIEN PROPERTY CUSTODIAN

PROCESS FOR CONDENSATION OF PRIMARY ALIPHATIC ALDEHYDES

Hans Machemer, Burghausen, Germany; vested in the Alien Property Custodian

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The invention refers to the production of glycoles and glycolic esters by condensation of aliphatic primary aldehydes with 3 till 6 carbon atoms.

There was found that carbides of the alkaline-earth metals per se or with oxydes of the alkaline earth metals resp.—hydroxides are excellently suitable as condensation agents. This fact is surprising, because milk of lime is known as condensation agent little suitable for the substituted aldehydes. During the reaction, according to the invention, indifferent solvents can be present, but it is not always necessary to use them. Also it is not out of question to carry on the process at over- or underpressure. There is no need of taking always pure aldehydes for starting materials. Suitable initial substances are also such, as they often fall on in the industry, which contain water and/or acids or compounds reacting like aldehydes.

If going out from aldehyde mixtures, corresponding mixtures of glycole half esters resp. glycoles are obtained. The half esters, being formed during the reaction cannot always be isolated, because they are occasionally saponified by the alkaline reacting condensation agent being present and especially—when water is present—in the leap of the reaction mixture so that 1,3-glycole and aliphatic carbon acids are obtained as the end product. The reaction is mostly done at boiling temperature under reflux but there can be worked also at lower temperatures, if more time is spent.

In the industry the process is mostly executed so, that the mixture of the starting materials is stirred with the condensation agent in the warmth and in a stirring apparatus—suitable supplied with a reflux condenser—till to the end of the condensation. It is also possible, to lead the starting materials by repumping continually over the condensation agent, f.e. granulated calcium carbide, whereby an equal generation of acetylene has to occur. The working up of the reaction mixture usually is executed in vacuum, after having siphoned off the condensate and having isolated the oil, reserved in the carbide sludge by extraction or solution of the lime sludge in cold diluted acid. The 1,3-glycole half ester obtained according to the invention are used especially as softening agents and solvents in the lacquer-industry.

Example 1

100 parts of weight of anhydrous butyric aldehyde are boiled under reflux and stirring with 20

parts of calcium carbide for four hours and a half, whereby the temperature of reaction vessel increases to 140°. Thereby nearly 1 part of acetylene is formed. If the reaction product is worked up, there are obtained:

5 parts of a fraction containing 2-ethyl-3n-propyl-acrolein, 12 parts of 2-ethyl-n-hexandiol-(1,3), 63 parts of 2-ethyl-n-hexandiol-(1,3)-butyrate boiling at 143° at 1 mm ($D_{20}=0.943$) and 7 parts in residue.

Example 2

A mixture of 100 parts of butyric aldehyde, 2,7 parts of water and 1,7 parts of crotonic aldehyde is brought in contact—by repumping—with 9 parts of calcium carbide which contains 1 part of calcium oxyde. Hereby the temperature is increased from 50° to 130° C. During the condensation 3 parts of acetylene are generated. After having finished the reaction—that is when no more butyric aldehyde is present, the mixture is cooled down, acidified with hydrochloric acid and then fractionated under vacuum. There are obtained:

19 parts of 2-ethyl-3-propyl-acrolein, 5 parts of 2-ethyl-hexandiol-(1,3) and 37 parts of 2-ethylhexandiol (1,3)-butyrate.

Example 3

100 parts of butyric aldehyde containing 0,5% of water are boiled with a mixture of 5 parts of calcium carbide and 0,05 parts of barium oxyde for 5 hours under reflux, whereby the temperature increases to 120°. During the fractionation under vacuum 15 parts of 2-ethyl-3-propyl-acrolein pass over. The contents of the reaction vessel is saponified with sodium lye, whereby 41 parts of 2-ethylhexandiol-(1,3) boiling at 132° at 11 mm ($n_{D,20}^2=1.453$, $D_{20}=0.935$) and 22 parts of butyric acid are obtained.

Example 4

100 parts of technical capronic aldehyde, which contains small quantities of caproic acid and about 0,6% of water are heated with 20 parts of calcium carbide for four hours till about 110°, whereby 3 parts of acetylene gas are generated. After having precipitated the mixture is filtered and the turbid solution containing calcium oxide is fractionated under vacuum. There are obtained until boiling at 121° at 6 mm 40 parts of 2n-butyl-3-n-amyl-acrolein and 2n-butyl-3n-amyl-propyl-alcohol and the caproic acid ester of it; boiling at 135–153° at 1 mm 10 parts of 2n-butyl-3n-amyl-allyl alcohol besides 35 parts of residue.

Example 5

100 parts of isopropyl-acetaldehyde are condensed at boiling temperature under reflux for about 3 hours in the presence of calcium carbide. There are obtained 29 parts of half ester boiling at 130-170° at 16 mm, which yields 2-isopropyl-3-isobutyl-propandiol-(1,3) boiling at 130° at 12 mm, if saponified.

Example 6

100 parts of butyric aldehyde, containing 0,5% of water are heated with 50 parts of xylene and 15 parts of calcium carbide under stirring for 8 hours till about 110°. Thereby 4 parts of acetylene are generated. When the oil, decanted from the sludge of carbide, is fractionated, there are

obtained: 5 parts of butyric aldehyde, 14 parts of 2-ethyl-3-propyl-acrolein and 38 parts of 2-ethyl-n-hexandiol-1,3-butyrate.

Example 7

5 100 parts of propionic aldehyde are boiled with 5 parts of calcium carbide for 6 hours under reflux. Then the mixture is distilled whereby 12 parts of methyl-ethyl-acrolein pass over. The residue consists in the main point in 2-methyl-10 pentandiol-1,3-propionate boiling at 120-125° at 15 mm. The ester is saponified with an excess of sodium lye, whereby 34 parts of 2-methyl pentandiol-1,3 boiling at 100-105° at 15 mm and 18 15 parts of propionic acid are obtained.

HANS MACHEMER.