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Method for Producing Aldehydes

Field of the Invention

This invention relates generally to perfumes and, more particularly, to a new process for the production of fatty aldehydes.

5 Prior Art

Lower aldehydes such as 1-octanal or 1-decanal, for example, are sought-after raw materials for the perfume industry. Their production from fatty alcohols, for example by oxidation with hypochlorite in the presence of 4-methoxy-2,2,6,6-tetramethyl piperidin-1-yloxy ("Tempo"), is known from
10 the prior art. The oxidation of the alcohols with air can be carried out in the presence of ruthenium or platinum catalysts. In addition, unsaturated alcohols can be isomerized to aldehydes under the influence of iron pentacarbonyl. The aldehydes are obtained from fatty acids by hydrogenation on oxidic copper catalysts of the Adkins type or by reaction
15 with per acids in the presence of titanium(IV) oxide. **RO 0111820** (Comb. Chim. Rimnicu Vilcea) reports on the use of heterogeneous oxidic copper catalysts for the dehydrogenation of fatty alcohols. Iron-doped copper catalysts are proposed for the same purpose in **EP 0320074 A1** (Engelhard). A classic method is the Rosenmund reaction in which acid
20 chlorides are hydrogenated to the corresponding aldehydes on Lindlar catalysts. Reference is made in this connection to the overview articles in **J. Am. Chem. Soc. 109, 3786 (1987)**, **J. Org. Chem. 52, 2259 (1987)** and **Tetrahedron Lett. 28, 4575 (1987)**.

Unfortunately, the known processes have the disadvantage that they
25 are equipment-intensive, give low yields and/or are characterized by unsatisfactory selectivities. Accordingly, the problem addressed by the present invention was to provide a new process which would reliably avoid



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the above-mentioned disadvantages of the prior art.

Description of the Invention

5 The present invention relates to a process for the production of aldehydes in which fatty alcohols are continuously dehydrogenated in the presence of oxidic copper/zinc catalysts at temperatures of 200 to 280°C and under pressures in the range from 10 mbar to 1 bar.

It has surprisingly been found that, by using the catalysts mentioned, fatty alcohols can be continuously dehydrogenated to fatty aldehydes in
10 yields of over 60% of the theoretical and with selectivities of over 90% of the theoretical.

Fatty alcohols

Suitable starting materials for the process according to the invention
15 are linear or branched, saturated or unsaturated primary alcohols which, in the interests of simplicity, are collectively referred to as fatty alcohols and which preferably correspond to formula (I):

R¹OH

(I)

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where R¹ is a linear or branched, saturated or unsaturated alkyl and/or alkenyl group containing 6 to 22, preferably 8 to 12 and more particularly 8 to 10 carbon atoms. Typical examples are caproic alcohol, caprylic alcohol, 2-ethylhexyl alcohol, capric alcohol, lauryl alcohol, isotridecyl
25 alcohol, myristyl alcohol, cetyl alcohol, palmitoleyl alcohol, stearyl alcohol, isostearyl alcohol, oleyl alcohol, elaidyl alcohol, petroselinyl alcohol, linolyl alcohol, linolenyl alcohol, elaeostearyl alcohol, arachyl alcohol, gadoleyl alcohol, behenyl alcohol, erucyl alcohol and brassidyl alcohol and the technical mixtures thereof obtained, for example, in the high-pressure
30 hydrogenation of technical methyl esters based on fats and oils or

aldehydes from Roelen's oxo synthesis and as monomer fraction in the dimerization of unsaturated fatty alcohols. Caprylic alcohol (1-octanol), 2-ethylhexanol and capric alcohol (1-decanol) and mixtures thereof are preferably used.

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Synthesis

The fatty aldehydes are preferably produced in a shaft reactor with a fixed catalyst bed. The oxidic copper/zinc catalysts are commercial Adkins catalysts, i.e. solids with a spinel structure which preferably contain
10 chromium, cadmium, cerium, barium, silicon and/or aluminium as other metal components. Basic copper/zinc/aluminum oxides are particularly preferred. The reaction normally takes place at temperatures of 200 to 280°C and preferably at temperatures of 240 to 260°C. The dehydrogenation is carried out either in the absence of pressure or under a
15 reduced pressure preferably in the range from 20 to 40 mbar. The liquid hourly space velocity (LHSV) is in the range from 1 to 3 and preferably in the range from 1.1 to 2.6 h⁻¹. The yield of fatty aldehydes is of the order of at least 60% and preferably 65 to 70% of the theoretical while selectivity is at least 90% and preferably 95 to 98%. It is advisable to carry out the
20 dehydrogenation in the presence of nitrogen as carrier gas.

Examples

In a continuous pressure reactor with a fixed catalyst bed, fatty alcohols were dehydrogenated to the corresponding aldehydes at a
25 temperature of 250°C and under pressures of 20 mbar to normal pressure. The test results are set out in Table 1. The aldehydes were obtained in yields of 60 to 70% and with selectivities of more than 90% of the theoretical.

Table 1**Continuous dehydrogenation of fatty alcohols**

Test parameter	1	2	3	4	5
Educt	1-Octanol	1-Decanol	1-Decanol	1-Octanol	1-Octanol
Product	1-Octanal	1-Decanal	1-Decanal	1-Octanal	1-Octanal
Catalyst metal	Cu/Zn/Al ¹⁾	Cu/Zn/Al ¹⁾	Cu/Zn	Cu/Zn	Cu/Si
LHSV [h ⁻¹]	1.1	1.1	2.6	1.8	0.7
Temperature [°C]	250	250	250	250	250
Pressure [mbar]	1000	20	42	40	17
Conversion educt [% of th.]	73	61	69	67	88
Yield product [% of th.]	66	57	67	64	84
Selectivity [% of th.]	90	93	97	97	95

¹⁾ Leuna catalyst 1962

CLAIMS

1. A process for the production of aldehydes, in which fatty alcohols are continuously dehydrogenated in the presence of oxidic copper/zinc catalysts at temperatures of 200 to 280°C and under pressures in the
5 range from 10 mbar to 1 bar.
2. A process as claimed in claim 1, characterized in that fatty alcohols corresponding to formula (I):

R¹OH**(I)**

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where R¹ is a linear or branched, saturated or unsaturated alkyl and/or alkenyl group containing 6 to 22 carbon atoms, are used.

3. A process as claimed in claims 1 and/or 2, characterized in that copper/zinc catalysts containing chromium, cadmium, cerium, barium,
15 silicon and/or aluminium as other metal components are used.
4. A process as claimed in any of claims 1 to 3, characterized in that the catalysts are arranged in a fixed bed.
5. A process as claimed in at least one of claims 1 to 4, characterized in that the dehydrogenation is carried out at temperatures in the range from
20 240 to 260°C.
6. A process as claimed in at least one of claims 1 to 5, characterized in that the dehydrogenation is carried out under pressures of 20 to 40 mbar.
7. A process as claimed in at least one of claims 1 to 6, characterized
25 in that the dehydrogenation is carried out at a liquid hourly space velocity (LHSV) of 1 to 3 h⁻¹.
8. A process as claimed in at least one of claims 1 to 7, characterized in that the dehydrogenation is carried out in the presence of nitrogen as carrier gas.