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Use of Aldehydes as Odorous Materials

Field of the Invention

This invention relates to the use of aldehydes obtainable by partial or complete hydroformylation of cyclooctadienes, excluding cyclooctane aldehyde, as perfumes.

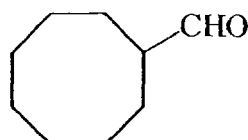
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Prior Art

The hydroformylation of cyclic dienes is known from the literature. For example, A. Spencer describes the hydroformylation of inter alia 1,3- and 1,5-cyclooctadiene in the presence of special rhodium catalysts in
10 **Journal of Organometallic Chemistry** 1997, 124, pages 85 to 91. JP 58/21638 describes a process for the production of dialdehydes in which unconjugated diolefins are reacted with hydrogen and carbon monoxide in a water-immiscible solvent in the presence of a rhodium catalyst.

There is no information in the prior art literature on the olfactory
15 properties of aldehydes or dialdehydes obtainable by hydroformylation of cyclooctadienes except for cyclooctane aldehyde. Only cyclooctane aldehyde (2a), which is described in **US 3,985,769** as a raw material for the production of acetal derivatives with perfume properties, is known for its olfactory properties which are described as "intensively green".

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(2a)

Judging by demand, many natural perfumes are available in totally inadequate quantities. Accordingly, it is clear that there is a constant



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demand in the perfume industry for new perfumes with interesting perfume notes in order to extend the range of naturally available perfumes and to be able to make the necessary adaptations to changing fashion trends and to satisfy the continuously increasing demand for odor enhancers for products
5 of everyday use, such as cosmetics and cleaning products.

In addition, there is generally a constant need for synthetic perfumes which can be favorably produced in a consistent quality and which have desirable olfactory properties, i.e. pleasant, near-natural and qualitatively new odor profiles of adequate intensity, and which are capable of
10 advantageously influencing the fragrance of cosmetic and consumer products. In other words, there is a constant need for compounds which have characteristic new odor profiles coupled with high staying power, intensity of odor and emanative power.

15 **Description of the Invention**

It has surprisingly been found that aldehydes obtainable by partial or complete hydroformylation of cyclooctadienes, except for cyclooctane aldehyde, have remarkable olfactory properties. Over and above their special odor characteristic, which is characterized by a broad range with
20 complex nuances, the compounds are distinguished by high staying and emanative power. In addition, they are eminently suitable as perfume boosters. A perfume booster is understood to be a substance which is capable of lastingly intensifying the olfactory impressions of the components of a multicomponent system, i.e. a mixture of two or more
25 perfumes.

The present invention relates to the use of aldehydes obtainable by partial or complete hydroformylation of cyclooctadiene, with the exception of cyclooctane aldehyde, as perfumes.

The present invention also relates to the use of aldehydes
30 obtainable by partial or complete hydroformylation of cyclooctadienes, with

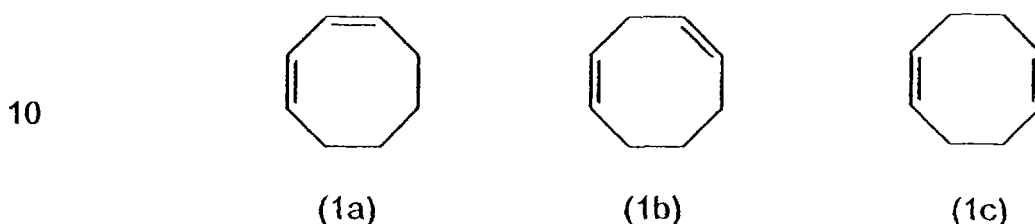
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the exception of cyclooctane aldehyde, as perfume boosters. 4-Cyclooctene aldehyde is particularly preferred for this use.

The aldehydes to be used in accordance with the invention are advantageously prepared by hydroformylation of cyclooctadienes. Any cyclooctadienes of which the olefinic double bonds are not immediately adjacent may be used. Accordingly, suitable starting materials are 1,3-cyclooctadiene (1a), 1,4-cyclooctadiene (1b) and 1,5-cyclooctadiene (1c):



The hydroformylation is a reaction known to the expert which was discovered by Roelen in 1938. In this reaction, alkenes are converted into aldehydes with carbon monoxide and hydrogen. The reaction is also known as oxosynthesis. Since, as mentioned above, cyclooctadienes are used as starting materials for the purposes of the present invention, the hydroformylation may be carried out in part or completely. In the case of partial hydroformylation, one olefinic double bond remains intact while only the other is hydroformylated; in the case of complete hydroformylation, two CHO groups are introduced into the molecule.

The odor profile of the hydroformylation products according to the invention is original and novel. In perfume compositions, they enhance harmony and emanation and also staying power, the particular dosage being adapted to the perfume note required taking the other constituents of the composition into account.

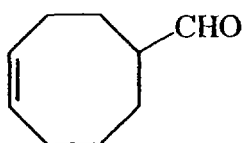
The fact that the hydroformylation products according to the invention have interesting perfume notes was not foreseeable and is confirmation of the general experience that the olfactory properties of known perfumes are not necessarily an indication of the properties of

structurally related compounds - in the present case cyclooctane aldehyde (2a) for example - or mixtures thereof because neither the mechanism of odor perception nor the influence of chemical structure on odor perception has been sufficiently researched, i.e. it cannot normally be predicted whether a modified structure or special mixing ratios of known perfumes lead at all to changes in the olfactory properties and whether these changes may be regarded as positive or negative.

By virtue of their odor profiles, the hydroformylation products according to the invention are also particularly suitable for modifying and enhancing known compositions. Particular emphasis is placed above all on their outstanding intensity of odor which contributes quite generally towards the refinement of compositions.

Also remarkable is the way in which the hydroformylation products according to the invention round off and harmonize the perfume notes of a broad range of known compositions without unpleasantly dominating them in any way.

4-Cyclooctene aldehyde (2b), which in undiluted form has an almost unpleasantly strong smell and of which the odor is reminiscent of freshly harvested potatoes, is most particularly suitable for use as a perfume and/or perfume booster in accordance with the invention. Accordingly, it is of particular advantage to use 4-cyclooctene aldehyde in air fresheners for example. In addition, it has been found that 4-cyclooctene aldehyde may be used with particular advantage for enhancing citrus notes in cleaning compositions. In this connection, reference is made by way of example to the following citrus composition:



(2b)

4-Cyclooctene aldehyde (2b), for which another chemical name is 5-formyl-1-cyclooctene, is generally obtained in the form of an (E,Z)-mixture in the course of its synthesis by hydroformylation of 1,5-cyclooctadiene, in other words the C=C double bond may be both E- and Z-configured, although a
5 mixture in which the Z configuration predominates is generally present. However, it may even be desirable to use the E- or Z-configured form in pure substance.

The quantities in which the hydroformylation products according to the invention are used in perfume compositions are between 0.001 and
10 70% by weight, based on the mixture as a whole. The hydroformylation products according to the invention and corresponding compositions may be used both for perfuming cosmetic preparations, such as lotions, creams, shampoos, soaps, salves, powders, aerosols, toothpastes, mouthwashes, deodorants, and in extract perfumery. They may also be used for
15 perfuming technical products and detergents and cleaning compositions, fabric softeners, textile treatment compositions and tobacco. For perfuming these various products, the compositions are added to them in an olfactorily effective quantity, more particularly in a concentration of 0.05 to 2% by weight, based on the product as a whole. However, these values
20 are not intended to represent limits because the experienced perfumist can still obtain effects with lower concentrations or can build up new complexes with even higher concentrations.

The following Examples are intended to illustrate the invention without limiting it in any way.

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Examples

1. Preparation of 4-cyclooctene aldehyde

2 Moles (216.36 g) of 1,5-cyclooctadiene (isomer mixture;
30 manufacturer: Acros; gas chromatographic purity: 99%) were introduced

into an autoclave together with 1.7 mmoles (1.175 g) of a rhodium catalyst with the formula $\text{Rh}(\text{CO})\text{Cl}(\text{PPh}_3)_2$ and 19 mmoles (5 g) of triphenyl phosphine and reacted with a 1:1 mixture of hydrogen and carbon monoxide with intensive stirring for 5 hours at 100°C under a pressure of 50 kg/cm² and in the absence of solvent. For working up, the contents of the reactor were filtered and distilled through a 20 cm Vigreux column. Fractionation into educt, monoaldehyde (4-cyclooctene aldehyde) and dialdehyde was carried out in a spinning band column. 110 g of 4-cyclooctene aldehyde (boiling point: 35°C/0.06 mbar) were obtained together with 12 g of cyclooctane-1,5-dialdehyde (boiling point: 101°C/0.06 mbar).

2. Application Examples

2.1. Citrus composition

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	Position	Parts by weight	Ingredient
	1	45	Citral AR
	2	80	Geranonitrile
	3	15	Citronellal
20	4	300	Orange oil, dist. white
	5	250	Orange oil, sweet
	6	10	Aldehyde C 08
	7	10	Aldehyde C 10
	8	70	Terpineol
25	9	30	Phenyl ethyl alcohol
	10	10	Geranyl acetate
	11	2	Dihydroisojasmonate
	12	70	Hexyl cinnamaldehyde, alpha
	13	x	Dipropylene glycol (DPG)
30	14	5	Peranat*

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15	8	Aldehyd 11-11*
16	10	Herbavert*
17	50	Melusat*
18	30	Cyclohexyl salicylat*
5	19	<u>y</u>
		<u>4-Cyclooctene aldehyde, 1% in DPG</u>
	1000	

The products marked with an asterisk are commercial products of Henkel KGaA (Düsseldorf).

10 Two variants of the composition were investigated:

	Parts by weight x	Parts by weight y
Variant 1	3	5
Variant 2	2	0

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Variant 1 was distinguished from variant 2 by the fact that the citrus aroma was found to be more natural, more rounded, more harmonic, more intense in odor and cleaner. By contrast, variant 2 appeared unclean and bitter and was more reminiscent of the odor of lemon pips.

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2.2. Raspberry aroma composition

	Position	Parts by weight	Ingredient
	1	10	Methyl naphthyl ketone, cryst.
25	2	1	Hexenyl acetate
	3	1	Allyl heptanoate
	4	2	Amyl butyrate
	5	9	Aldehyde C 16 so-called
	6	2	Frambinone methyl ether
30	7	80	Oxyphenylone

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	8	2	Anisyl acetate
	9	10	Styrollyl acetate
	10	10	Citronellol, pure
	11	1	DMBCA (dimethyl benzyl carbiny acetate)
5	12	0.5	Floraline Jasmin 73
	13	30	Benzyl acetate
	14	10	Dihydroisojasmonate
	15	2	Isoraldein 70
	16	5	Ionone pure 100
10	17	30	Vanillin
	18	2	Maltol
	19	5	Methyl cinnamate
	20	0.5	Jasmacyclat*
	21	1	Herbavert*
15	22	5	Floramat*
	23	30	Cyclohexyl salicylat*
	24	x	Dipropylene glycol (DPG)
	25	y _____	4-Cyclooctenaldehyde 1% in DPG
		1000	

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The commercial products marked with an asterisk are perfumes of Henkel KGaA.

Two variants of the composition were investigated:

25		Parts by weight x	Parts by weight y
	Variant 3	749	751
	Variant 4	2	0

Variant 3 was distinguished from variant 4 by a more natural, fresher
30 and fruitier raspberry note. Even after 24 hours, its strong and fresh green

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note still had the same intensity of odor emanating from the sniffing strip. In addition, the perfume spread very intensively and quickly in the test room. By contrast, variant 4 was non-typical, faint and flat in its effect, did not have any room effect and, after 24 hours, could only be detected as a

5 raspberry ketone/vanillin note.

CLAIMS

1. The use of aldehydes obtainable by partial or complete hydroformylation of cyclooctadienes, except for cyclooctane aldehyde, as perfumes.
- 5 2. The use of 4-cyclooctene aldehyde as a perfume.
3. The use of aldehydes obtainable by partial or complete hydroformylation of cyclooctadienes as a fragrance booster.
4. The use of 4-cyclooctene aldehyde as a fragrance booster.
5. The use of aldehydes obtainable by partial or complete hydroformylation of cyclooctadienes, except for cyclooctane aldehyde, in
10 cosmetic preparations, technical products or in alcohol-based perfumery.
6. The use of 4-cyclooctene aldehyde in cosmetic preparations, technical products or alcohol-based perfumery.