

Methylcyclotetradec-5-en-1-ones



The invention relates to methylcyclotetradec-5-en-1-ones and to scent compositions comprising at least one
5 methylcyclotetradec-5-en-1-one.

Although G. Ohloff, Fortschritte der chemischen Forschung [Advances in Chemical Research], Vol. 12/2, 201 states that macrocyclic carbonyl compounds having
10 more than 13, but fewer than 19, carbon atoms are involved in achieving a musk odor, all commercial musk scents have ring sizes of 15, 16 or 17 carbon atoms. Extremely little is known about the olfactory properties of fourteen-membered ring ketones, and only
15 then in isolated cases.

US-A 4,183,965 describes the use of a mixture of 2- and 3-cyclotetradecen-1-one for reducing the bitter taste of foods. The compounds can also be used in perfumery
20 and have a sweet, musk-like, exaltone-like, waxy, rooty odor.

JP-A 55-66534 describes the synthesis of 5-cis-cyclotetradecen-1-one having a musk-like character by
25 heating 1-vinyl-3-cis-cyclododecen-1-ol with an alkali metal or alkali metal hydride. E. Yoshi and S. Kimoto: Chem. Pharm. Bull 17, 629, 1969 and, subsequently, M. Karpf and A. S. Dreiding: Helvetica Chimica Acta, Vol. 58(8), 2409, 1975 describe the synthesis of a
30 mixture of cis- and trans-3-methylcyclotetradec-2-en-1-ones and 3-methylcyclotetradec-3-en-1-ones. Olfactory properties of these compounds are not given.

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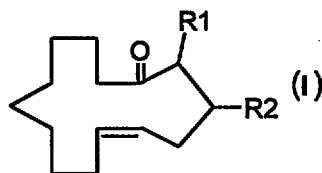
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REPLACED SHEETS		SG
☒ Description	: paged 01 to paged 22	
☒ Claim(s)	: paged 23 to paged -	
☒ Drawing(s)	: paged - to paged -	
☒ Abstract	: paged 24 to paged -	

The preparation of 3-methyl-trans-cyclopentadec-5-enone is described by R.W. Thies and K.P. Daruwala: J.Org.Chem. 1987, 52, 3798 by treatment of trans- or cis-1-(1-propenyl)-trans-cyclotridec-3-en-1-ol with
5 potassium hydride in hexamethylphosphoramide.

US-A 5,354,735 describes cis- and trans-isomers of 3-methylcyclopentadec-5-en-1-one as scent constituents having musk-like properties. The cis-isomer is
10 stronger, more elegant and has more of a musk odor and less of an animal odor than the trans-isomer, which has more of a nitromusk character and ambrette seed odor.

Surprising, it has now been found that compounds of the
15 formula I



in which R^1 and R^2 are hydrogen or methyl, with the proviso that, when R^1 is methyl, R^2 is hydrogen, and when R^1 is hydrogen, R^2 is methyl, it being possible for
20 the compounds of the formula I to be in the Z- and/or in the E-form, have a strong musk-like, i.e. nitromusk-like, powdery, fruity odor, and at the same time have a low threshold value and very good staying power.

25 A particularly preferred compound of the formula I is E-3-methylcyclotetradec-5-en-1-one, which, surprisingly, has an odor which is more than ten times stronger than the corresponding Z-compound, Z-3-methylcyclotetradec-5-en-1-one. E-3-Methylcyclotetradec-5-en-
30 1-one has a gas-chromatographic threshold value of



0.2 ng while Z-3-methylcyclotetradec-5-en-1-one has one of 2.2 ng.

5 The compounds of the formula I can, like the known musk scents, be used generally, i.e. they harmonize with a large number of natural and synthetic products which are frequently used in scent compositions. Particularly in the base note, they achieve interesting effects in combination with amber-like and woody accords, such as
10 patchouli oil, and cedarwood and sandalwood scents. Floral body (middle) notes impart elegance and radiance to the compounds of the formula I. Some examples of classes of substance which harmonize particularly well are:

15

Natural products, such as oakmoss absolute, geranium oil, jasmine absolute, patchouli oil, rose oil, sandalwood oil, vetiverol and ylang ylang oil, etc.

20 Alcohols, such as citronellol, Ebanol®, geraniol, linalool, phenyl ethyl alcohol and Sandalore®, etc.

Aldehydes and ketones, such as Florozone® (3-(4-ethylphenyl)-2,2-dimethylpropional), hydroxycitronellal
25 Iso-E-Super®, Isoraldein®, maltol, methyl cedryl ketone, methylionone and vanillin, etc.

Ethers and acetals, such as ambrox, geranyl methyl ether, rose oxide and Spirambrene®, (2',2',3,7,7-
30 pentamethyl-spiro[bicyclo[4.1.0]heptan-2-5'-[1,3]dioxane]), etc.



Esters and lactones, such as Berryflor®, γ -decalactone and γ -undecalactone, etc.

The compounds I can be used in the preparation of
5 compositions and, as the above list shows, using a broad range of known scents and scent mixtures.

The advantageous properties of the compounds of the formula I permit broad and diverse use firstly in sweet
10 oriental creations, and secondly in the fragrance trends "fougère", "chypre" and "floral".

Because of the low threshold values and good staying power, the compounds of the formula I can be used both
15 in luxury perfumery, in compositions for cosmetic products, and for mass-produced products, such as detergents.

The compounds of the formula I can be used within wide
20 concentration limits, which can range, for example, from about 0.1% in detergents to about 40% by weight in alcoholic solutions. Preferred concentrations are between 3 and 20% by weight. Concentrations outside the upper limit are also possible since the experienced
25 perfumer can also achieve novel effects using lower or higher concentrations. Compositions which comprise one or more of the compounds of the formula I can be used for all types of perfumed consumer goods, such as eaux de cologne, eaux de toilette, extraits, lotions,
30 creams, shampoos, soaps, ointments, powders, deodorants, detergents and other household products etc.

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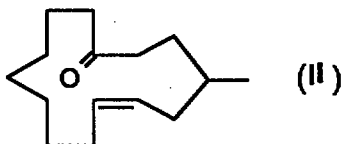


In the preparation of compositions, the compounds of the formula I can be used together with other scents or scent mixtures in a known manner, as described, for example, by W.A. Poucher, *Perfumes, Cosmetics, Soaps*, Vol. 2, 7th edition Chapman and Hall, London 1974.

The compounds of the formula I can be prepared by various methods.

- 10 The compound of the formula I in which R^1 is H and R^2 is CH_3 is prepared by a first method in a mixture with a compound of the formula II

15



- i.e. cis- and trans-4-methylcyclotetradec-6-en-1-one. For this, (4-carboxy-3-methylbutyl)triphenylphosphonium bromide is subjected to a Wittig reaction, for example by treatment with potassium t-butoxide in tetrahydrofuran and subsequent addition of methyl 9-oxononanoate. The resulting product, dimethyl 3-methyltetradec-5-enedioate is subjected to an acyloin condensation and then treated with acetic anhydride/pyridine. The resulting mixture of mainly Z-4-methyl-2-oxocyclotetradec-6-enyl acetate and Z-3-methyl-14-oxocyclotetradec-5-enyl acetate is treated with calcium in ammonia at low temperature ($-30^{\circ}C \rightarrow -70^{\circ}C$), the excess calcium being destroyed using bromobenzene.

This method gives a mixture of:

E-3-methyl-cyclotetradec-5-enone	11%
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Z-3-methyl-cyclotetradec-5-enone	35%
Z-4-methyl-cyclotetradec-6-enone	49%

Odor: strongly musk-like (nitromusk), powder-like.

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A second method of preparing the compound I ($R^1=H$, $R^2=CH_3$), preferably in the trans-form, starts with 2-chlorocyclododecanone or 2-bromocyclododecanone, which can be obtained in one stage from cyclododecanone
10 (JP 491 093 39, EP-A-051 233). Treatment of 2-chlorocyclododecanone with lithium carbonate in N-methylpyrrolidone at reflux temperature gives a mixture of:

5% of Z-cyclododec-2-en-1-one
15 6% of E-cyclododec-2-en-1-one
13% of cyclododecanone
57% of E-cyclododec-3-en-1-one
16% of Z-cyclododec-3-en-1-one

20 The abovementioned mixture is treated with 1-bromo-1-propenylmagnesium bromide in tetrahydrofuran. This gives a mixture of mainly cis/trans-1-(1-propenyl)cyclododecen-3-en-1-ol. After treatment with sodium hydride in N-methylpyrrolidone, this
25 compound gives a mixture of E-3-methylcyclotetradec-5-en-1-one, Z-3-methylcyclotetradec-5-en-1-one (E:Z = 3:1) and the two diastereomeric 3-methyl-4-vinylcyclododecanones.

30 The mixture has an odor which is very strongly musk-like (nitromusk), powdery, linear, like fresh laundry (dried in the sun). The weak, woody odor of the two diastereomeric 3-methyl-4-vinylcyclododecanones is completely concealed by the two musk compounds E-3-



methycyclotetradec-5-en-1-one and Z-3-methyl-
cyclotetradec-5-en-1-one according to the invention.

5 A similar mixture of E- and Z-3-methylcyclotetradec-5-
en-1-one can be obtained by pyrolysis of the silyl
ether of cis/trans propenylcyclododecen-3-en-1-ol.

The compounds of the formula I ($R^1=CH_3$, $R^2=H$) can be
prepared as follows:

10

A mixture of mainly E-cyclododec-3-en-1-one (74%) and
Z-cyclododec-3-en-1-one (19%) is treated with
isopropenylmagnesium bromide in tetrahydrofuran, giving
mainly E-1-isopropenylcyclododecen-3-en-1-ol. The
15 purified E-1-isopropenylcyclododecen-3-en-1-ol is
treated with potassium hydride in N,N-dimethylacetamide
in the presence of 18-crown-6, giving a mixture of
diastereomeric 2-methyl-4-vinylcyclododecanone and E-2-
methycyclotetradec-5-en-1-one.

20

Odor of E-2-methycyclotetradec-5-en-1-one: musk
(nitromusk), powdery, sweet.

25 The invention is further illustrated by reference to
the examples below, but without limiting it.

Example 1

143 g (0.313 mol) of (4-carboxy-3-methylbutyl)-
30 triphenylphosphonium bromide are pulverized and
introduced into 630 ml of tetrahydrofuran. The
resulting suspension is stirred for 10 minutes, then
cooled to -20°C and slurried rapidly with 70 g



(0.625 mol) of potassium t-butoxide in 315 ml of tetrahydrofuran. The temperature increases to 0°C and the reaction mixture turns orange. The mixture is then stirred for 45 minutes at between -5°C and 0°C. The mixture is then cooled to -20°C, and 76 g (purity 70%) (0.285 mol) of methyl 9-oxononanoate are added. The temperature increases to -1°C. The mixture is left to warm to room temperature (1 hour and 30 minutes) and is stirred for a further hour at 40°C. The reaction mixture is poured onto 1.5 l of iced water, adjusted to a pH of 14 using 25 ml of 30% NaOH and extracted with 2 x 700 ml of ether. The pH of the aqueous phases is adjusted to 2-3 using 100 ml of ortho-phosphoric acid, and the phases are extracted with 2 x 500 ml of ether. The organic phase is washed with 300 ml of water and 300 ml of saturated sodium chloride solution, dried over Na₂SO₄ and concentrated by evaporation. The crude product 102.9 g is diluted with 360 ml of methanol, 3.4 g of p-toluenesulfonic acid are added thereto, and the mixture is refluxed for 3 hours and 30 minutes. An excess of NaHCO₃ (solid) is then added and the mixture is concentrated by evaporation. The crude product (108.9 g) is chromatographed over 1 kg of silica gel 60 (Merck) (0.040 mm - 0.063 mm) with 6 l of hexane/ether 4:1 and 2 l of hexane/ether 3:1. 57.3 g of dimethyl Z-3-methyltetradec-5-enedioate are obtained.

Spectroscopic data for the product:

IR (liquid): 3004; 2928; 2855; 1740; 1458; 1436;
1364; 1251; 1198; 1168; 1011.

NMR: (CDCl₃, 200 MHz) 5.4 (2H) m; 3.66 (6 H) s.

MS: 298 (0.8); 266 (20); 248 (7); 235 (34);



224 (60); 206 (10); 192 (28); 175 (8);
164 (19); 150 (25); 136 (19); 123 (18);
109 (38); 95 (66); 87 (30); 81 (94); 75
(69); 68 (69); 59 (75); 55 (100); 41
(88); 29 (27).

5

Example 2

A dry apparatus with oil bath is charged with 2 l of
10 xylene, and argon is passed through for 30 minutes. The
oil bath is heated to 148°C. From an internal
temperature of 100°C, 17.2 g (0.750 mol) of sodium are
added in portions. A solution of 56 g (0.188 mol) of
15 dimethyl Z-3-methyltetradec-5-enedioate in 150 ml of
xylene is then added dropwise over the course of 4
hours.

The internal temperature increases to 134°C. The
mixture is then stirred for 30 minutes at this
20 temperature and then cooled to room temperature, and
120 ml of EtOH and 50 ml of water are added dropwise.
The organic phase is washed with 400 ml of water and
200 ml of saturated sodium chloride solution, dried
over Na₂SO₄ and concentrated by evaporation. In this
25 way, 36.6 g of crude product are obtained. This crude
product is dissolved in 75 ml of pyridine, 15.4 g of
acetic anhydride are added, and the mixture is stirred
for 4 hours at 80°C. The product is poured onto 400 ml
of iced water, adjusted to pH 2 using concentrated
30 hydrochloric acid and extracted with 2 x 200 ml of
ether. The organic phases are washed with water and
saturated sodium chloride solution, and dried over
sodium sulfate and concentrated by evaporation.



This method gives 41.5 g of crude product, which is chromatographed over 1 kg of silica gel 60 (Merck) (0.040 mm - 0.063 mm). 30.9 g of a mixture of mainly Z-4-methyl-2-oxocyclotetradec-6-enyl acetate and Z-3-methyl-14-oxocyclotetradec-5-enyl acetate are obtained.

Spectroscopic data for the mixture:

IR (liquid): 3006; 2928; 2857; 1746; 1727; 1461; 1373; 1236; 1087; 1026.

10

NMR: (CDCl₃, 200 MHz) 5.45 (2H) m; 5.1 (2H) m; 2.15 (3H) s.

15 MS: 280 (1); 238 (9); 220 (9); 202 (3); 191 (1); 177 (4); 163 (4); 149 (5); 135 (7); 121 (12); 111 (16); 95 (20); 81 (28); 67 (18); 55 (28); 43 (100); 29 (8).

20

Example 3

1.4 l of ammonia are added, at -50°C and over the course of 20 minutes, to 35.8 g (0.893 mol) of calcium, and the mixture is stirred at -60°C for 20 minutes. 30 g of a mixture of mainly Z-4-methyl-2-oxocyclotetradec-6-enyl acetate and Z-3-methyl-14-oxocyclotetradec-5-enyl acetate in 330 ml of tetrahydrofuran are added dropwise at -50°C over the course of 2 hours, and the mixture is stirred at -70°C for 15 minutes. 160 ml of bromobenzene are then added dropwise over the course of 30 minutes. The mixture is left to warm to room temperature, and the ammonia is removed by evaporation. The product is then poured onto ice, acidified to pH 3 using ortho-phosphoric acid and

35 A 12475/11.08.99/RWS

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extracted with ether. The organic phase is washed with water and saturated sodium chloride solution, dried over Na_2SO_4 , and concentrated by evaporation. The crude product (39.8 g) is chromatographed over 800 g of silica gel 60 (Merck) (0.040 - 0.063 mm). This method gives 13.7 g of a mixture of:

	E-3-methyl-cyclotetradec-5-enone	11%
	Z-3-methyl-cyclotetradec-5-enone	35%
10	Z-4-methyl-cyclotetradec-6-enone	49%

Odor of the mixture: musk (nitromusk), powdery.

Odor of E-3-methylcyclotetradec-5-enone: musk, powdery, animal, ambergris-like.

The individual compounds could be obtained in pure form by additional chromatography over silica gel (0.040 - 0.063 mm) using 10% silver nitrate.

Spectroscopic data of: Z-3-methylcyclotetradec-5-en-1-one:

IR: (liquid): 3008; 2929; 2859; 1710; 1460; 1408; 1369; 1047; 718.

^1H -NMR: (CDCl_3 , 200 MHz) 5.46 (2H) m; 1.0 (3H) d; $J = 7.5$ Hz.

^{13}C -NMR: (CDCl_3) 211.2 (s); 131.6 (d); 126.7 (d); 49.6 (t); 40.2; (t) 32.8 (t); 30.6 (d); 27.3 (t); 26.1 (t); 25.6 (t); 25.0 (t); 24.7 (t); 21.1 (t); 20.1 (q).



MS: 222 (25); 207 (5); 193 (4); 179 (11);
164 (17); 147 (8); 135 (17); 121 (19);
109 (33); 95 (58); 81 (100); 68 (94);
55 (89); 41 (94); 29 (25).

5

Spectroscopic data of Z-4-methylcyclotetradec-6-en-1-one:

IR (liquid): 3007; 2928; 2858; 1711; 1461; 1408;
1375; 1287; 1124; 1046; 712.

10

¹H-NMR: (CDCl₃, 200 MHz) 5.35 (1H) m; 5.48 (1H) m;
0.96 (2H) d; J = 7.5 Hz.

¹³C-NMR: (CDCl₃) 212.1 (s); 130.8 (d); 127.7 (d);
15 40.2 (t); 39.7 (t); 33.4 (d); 33.4 (t);
30.8 (t); 27.0 (t); 26.7 (t); 26.1 (t);
25.5 (t); 25.2 (t); 23.2 (t); 19.6 (q).

MS: 222 (33); 204 (4); 193 (3); 179 (15);
20 165 (14); 147 (10); 135 (12); 125 (21);
111 (47); 98 (56); 81 (60); 67 (55);
55 (100); 41 (70); 29 (23).

25 Spectroscopic data of E-3-methylcyclotetradec-5-en-1-one:

IR (liquid): 2928; 2856; 1708; 1458; 1441; 1365; 970

H-NMR: (CDCl₃, 400 MHz) 5.32 (2H) m; 2.86 (1H) dd,
J = 17 Hz, J = 2 Hz; 2.33 (1H) m; 0.95
30 (3H) d; J = 6.6 Hz.

¹³C-NMR: (CDCl₃) 212.4 (s); 132.8 (d); 129.9 (d);
46.2 (t); 42.9 (t); 31.1 (t); 29.0 (d);
27.2 (t); 26.5 (t); 25.2 (t); 24.8 (t);
35 24.5 (t); 23.3 (t); 21.1 (q).



MS: 222 (69); 207 (14); 193 (6); 179 (15);
164 (34); 154 (1); 147 (12); 135 (30);
123 (26); 109 (41); 95 (69); 81 (100);
5 67 (76); 55 (63); 41 (57); 28 (16).

Example 4

100 g of lithium carbonate (1.35 mol, pulverized) and
10 260 g (1.2 mol) of 2-chlorocyclododecanone are added to
1.2 l of N-methylpyrrolidone. The mixture is heated to
180° - 185°C with stirring, and CO₂ is eliminated (time:
3 hours). The crude mixture is cooled, poured onto
2.5 l of water and extracted by shaking three times
15 with hexane, and the organic phase is washed three
times with water, dried and concentrated by
evaporation. The crude product (238 g) is distilled
under a high vacuum (0.1 mm). After an initial fraction
(4.9 g), 105 g of a product having a boiling point of
20 from 89 to 95°C/0.1 mm are obtained. The gas
chromatographic analysis shows:

5% of Z-cyclododec-2-en-1-one
6% of E-cyclododec-2-en-1-one
13% of cyclododecanone
25 57% of E-cyclododec-3-en-1-one
16% of Z-cyclododec-3-en-1-one

Spectroscopic data of Z-cyclododec-3-en-1-one:

¹³C-NMR: (CDCl₃) 211.0 (s); 132.0 (d); 122.9 (d);
30 43.4 (t); 37.7 (t); 26.6 (t); 26.3 (t);
24.3 (t); 24.1 (t); 23.5 (t); 23.0 (t);
22.6 (t).

MS: 180 (62); 162 (6); 151 (19); 137 (25); 123



- 14 -

(25); 111 (52); 98 (100); 81 (68); 67 (82);
54 (84); 41 (60); 27 (12).

Spectroscopic data of E-cyclododec-3-en-1-one:

5 H-NMR: (CDCl₃, 400 MHz) 5.7 - 5.61 d,t,t (1H); J = 15.3
Hz; J = 1.2 Hz; J = 7.4 Hz; 5.34 - 5.43 d,t,t
(1H); J = 15.2 Hz; J = 1.2 Hz; J = 7.6 Hz; 3.04
(2H) d; J = 7.6 Hz; 2.48 (2H) t; J = 6.8 Hz;
2.03 (2H) m.

10

¹³C-NMR: (CDCl₃) 209.7 (s); 136.3 (d); 122.8 (d);
48.3 (t); 39.6 (t); 32.2 (t); 26.3 (t);
25.4 (t); 24.9 (t); 24.1 (t); 23.9 (t);
15 22.1 (t).

MS: 180 (68); 162 (62); 151 (17); 137 (23); 123
(23); 111 (51); 98 (100); 81 (63); 67 (80);
54 (86); 41 (61); 27 (12).

20

Example 5

8.26 g of magnesium (0.34 mol) are activated with a few
crystals of iodine, 25 ml of tetrahydrofuran are added,
25 and 41 g (0.34 mol) of 1-bromo-1-propene (cis/trans
mixture) dissolved in 120 ml of tetrahydrofuran are
slowly added dropwise at 70°C (dropping time 1 hour and
30 minutes). The mixture is stirred at this temperature
for 3 hours. It is then cooled to 0°C, and 51.2 g of a
30 mixture of mainly E-cyclododec-3-en-1-one (62%),
Z-cyclohex-3-en-1-one (18%) and E-cyclododec-2-en-1-one
(7%), prepared as in Example 4, dissolved in 100 ml of
tetrahydrofuran are added dropwise over the course of
30 minutes. The mixture is then stirred at room
35 temperature for 1 hour and 30 minutes, and saturated

A 12475/11.08.99/RWS

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ammonium chloride solution cooled in ice and water are added, and 100 ml of ether and 37 g of phosphoric acid are added. The phases are separated and extracted twice with ether. The organic phase is washed with saturated sodium chloride solution, dried and concentrated by evaporation. 60.7 g (96%) of crude product are obtained, which is a mixture of mainly 1-cis/1-trans-propenylcyclododecen-3-en-1-ol. To characterize the compounds formed, 3.6 g of the crude product were chromatographed over 110 g of silica gel 60 (Merck) (0.04 - 0.063 mm) (elution: hexane/ether, firstly 9:1, then 2:1).

Spectroscopic data of (1E,3E)-1-(1-propenyl)cyclododecen-3-en-1-ol:

H-NMR: (CDCl₃, 400 MHz) 5.71 - 5.51 (3H) m; 5.51 - 5.4 (1H) m; ABX System: 2.33 (1H) dd, J = 7.6; J = 14 Hz, 2.25 (1H) dd J = 6 Hz, J = 14 Hz; 2.1 (2H) dd; J = 5.6; J = 5.6; 1.7 (3H) d, J = 5 Hz.

¹³C-NMR: (CDCl₃) 138.1 (d); 134.7 (d); 125.3 (d); 122.8 (d); 74.7 (s); 43.0 (t); 37.1 (t); 33.3 (t); 28.6 (t); 27.0 (t); 26.0 (t); 25.5 (t); 24.3 (t); 19.0 (t); 17.8 (q).

MS: 222 (2); 207 (17); 204 (64); 189 (7); 179 (9); 175 (10); 161 (12); 147 (16); 133 (26); 119 (33); 105 (51); 97 (60); 91 (58); 84 (69); 79 (55); 69 (100); 55 (29); 41 (35); 29 (6).

Spectroscopic data of (1-Z,3E)-1-(1-propenyl)cyclododecen-3-en-1-ol:

H-NMR: (CDCl₃, 400 MHz) 5.69 - 5.3 (4H) m, 2.4 (2H) d,



J = 6.5 Hz, 2.11 (2H) dd J = 6 Hz, J = 6 Hz,
1.9 (3H) d J = 5.5 Hz.

¹³C-NMR: (CDCl₃) 136.2 (d); 134.9 (d); 126.5 (d); 125.3
5 (d); 75.8 (s); 44.6 (t); 37.8 (t); 33.3 (t);
28.5 (t); 27.1 (t); 26.0 (t); 25.1 (t); 24.3
(t); 19.1 (t); 14.5 (q).

MS: 222 (1); 208 (14); 204 (27); 189 (3); 179 (7);
10 175 (6); 166 (5); 161 (6); 151 (9); 147 (8);
133 (12); 124 (12); 119 (16); 105 (25); 97
(44); 91 (28); 84 (51); 79 (29); 69 (100); 55
(20); 41 (25); 29 (4).

15

Example 6

A dried apparatus is charged with 11.1 g of propenylcyclododecen-3-en-1-ol, prepared as in Example 5, (crude product) in 150 ml of N-methylpyrrolidone,
20 and 4.8 g of sodium hydride (55%) are added. Hydrogen starts to evolve at a moderate rate, and the temperature increases to 30°C. The mixture is then stirred for 5 hours at 85°C and cooled, and 20 ml of water are added dropwise. The product is poured onto
25 200 ml of iced water, adjusted to pH 5 with 10 ml of phosphoric acid and extracted with ether. The organic phase is washed with water and saturated sodium chloride solution, dried and concentrated by evaporation. The product (13.6 g) was chromatographed
30 (380 g of silica gel, 0.04 - 0.063 mm: elution: hexane/ether 19:1 and 8:1). This gives 3.6 g of product in addition to 2.7 g of starting material. The product consists of a mixture of mainly E-3-methylcyclotetradec-5-en-1-one, Z-3-methylcyclotetradec-5-en-
35 1-one (E:Z = 3:1) and erythro and threo 3-methyl-4-vinylcyclododecanone. The mixture has an odor which is
A 12475/11.08.99/RWS



very strongly musk-like (nitromusk), powdery, linear, like fresh laundry (dried in the sun). The individual compounds could be purified by additional chromatography over 10% NO₃Ag silica gel.

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Spectroscopic data of 3-methyl-4-vinylcyclododecanone (1,diastereomer):

IR (liquid): 3074; 2932; 2866; 1707; 1637; 1467;
1445; 1368; 1323; 1173; 1037; 994; 911.

10

H-NMR: (CDCl₃, 200 MHz 5.7 (1H) m; 5.08 (1H) m;
5.0 (1H) m; 2.96 (1H) dd; J = 18 Hz;
J = 11 Hz; 0.84 (3H) d; J = 7.5 Hz.

15

¹³C-NMR: (CDCl₃) 211.6 (s); 141.3 (d); 114.8 (t);
44.4 (t); 43.4 (t); 41.1 (d); 31.8 (d);
26.0 (t); 24.4 (t); 23.5 (t); 23.0 (t);
22.7 (t); 22.5 (t); 14.9 (q).

20

MS: 222 (1); 207 (2); 193 (5); 165 (4); 151
(8); 37 (14); 123 (17); 109 (29); 95
(42); 81 (60); 67 (90); 55 (98); 41
(100); 29 (27).

25

Spectroscopic data of 3-methyl-4-vinylcyclododecanone (2,diastereomer):

H-NMR: (CDCl₃, 400 MHz; 5.55 (1H) m; 5.08 (1H) m;
5.05 (1H) m; 0.9 (3H) d; J = 7 Hz.

30

¹³C-NMR: (CDCl₃) 211.7 (s); 138.6 (d); 116.4 (t);
49.6 (t); 43.10 (d); 38.2 (t); 32.1 (d);
30.7 (t); 26.0 (t); 23.87 (t); 23.85 (t);
23.5 (t); 22.8 (t); 21.7 (t); 16.0 (q).



MS: 222 (15); 207 (22); 193 (28); 180 (6);
179 (24); 175 (27); 165 (25); 151 (31);
137 (54); 123 (58); 109 (70); 95 (76);
81 (84); 67 (95); 55 (100); 41 (81); 29
(15).

5

Example 7

7 g (0.3 mol) of magnesium are coated with a layer of a
small amount of tetrahydrofuran (50 ml), and 3 g of 2-
10 bromopropene in 28 ml of tetrahydrofuran are added. The
mixture is warmed briefly, and the reaction starts.
27 g of 2-bromopropene dissolved in 160 ml of
tetrahydrofuran are then added dropwise over the course
of 90 minutes. Here, an ice bath is used for cooling,
15 so that the temperature remains between 55°C and 60°C.
The mixture is then refluxed for 20 minutes and cooled
(20°C), and 40 g (0.222 mol) of a mixture of mainly
E-cyclododec-3-en-1-one (74%) and Z-cyclododec-3-en-1-
one (19%) dissolved in 50 ml of tetrahydrofuran are
20 added dropwise over the course of 1 hour. The
temperature must not exceed 35°C. The mixture is then
stirred for 20 minutes at room temperature. The
reaction product is poured onto a mixture of ice/water
and ammonium chloride, extracted with methyl t-butyl
25 ether, washed with water and saturated sodium chloride
solution, dried over magnesium sulfate and concentrated
by evaporation. The crude product (48 g) was
chromatographed (hexane, methyl t-butyl ether 9:1).
This method gives 37 g of E-1-isopropenylcyclododecen-
30 3-en-1-ol. Recrystallization gives a product (33 g)
with a purity of 95%.

Spectroscopic data of E-1-isopropenylcyclododecen-3-
en-1-ol:



IR (KBr): 3285; 2988; 2932; 2861; 1641; 1448; 1396;
1368; 1212; 1024; 1003; 981; 898; 700.

5 H-NMR: (CDCl₃, 400 MHz); 5.43-5.73 (2H) m ; 4.8-5
(2H) m; 1.8 (3H) m.

¹³C-NMR: (CDCl₃) 150.22 (s); 134.67 (d); 125.71 (d);
110.30 (t); 76.66 (s); 41.27 (t); 34.64 (t);
33.24 (t); 28.42 (t); 26.98 (t); 26.00 (t);
10 24.93 (t); 24.42 (t); 19.22 (t); 18.81 (q).

Example 8

200 ml of N,N-dimethylacetamide, 34 g of 18-crown-6
15 (Fluka) are added to 25 g (0.125 mol) of potassium
hydride (20% in oil). 18 g (0.085 mol) of E-1-
isopropenylcyclododecen-3-en-1-ol (purity 95%) are
then added and heated rapidly to 120°C, and an orange-
red solution forms, which is maintained at 120°C for 1
20 minute and then left to cool to room temperature. The
reaction mixture is poured onto water, ice and citric
acid and extracted with hexane. The organic phase is
washed until neutral with water and saturated sodium
chloride solution, dried over magnesium sulfate and
25 concentrated by evaporation. The crude product (20 g)
is chromatographed with hexane and methyl t-butyl
ether. This gives 4.2 g of a mixture of diastereomeric
cyclododecanone, 6.2 g of a mixture of diastereomeric
2-methyl-4-vinylcyclododecanone, E-2-methylcyclotetra-
30 dec-5-en-1-one and 3 g of pure E-2-methylcyclotetradec-
5-en-1-one.

Spectroscopic data of the mixture of diastereomeric
2-methyl-4-vinylcyclododecanone:



- 20 -

IR (liquid): 3075; 2931; 2864; 1705; 1639; 1465; 1444;
1360; 912.

5 H-NMR: (CDCl₃, 200 MHz) 5.25-5.65 (1H)m; 5.1-4.9
(2H)m; 1.11 (3H) d; J = 6.5 Hz.

10 MS: 222 (14); 207 (7); 193 (24); 180 (8); 179
(17); 175 (19); 175 (22); 150 (75); 137
(27); 123 (53); 109 (77); 95 (83); 81
(100); 67 (90); 55 (99); 41 (80); 29
(15).

Spectroscopic data of E-2-methylcyclotetradec-5-en-1-one:

15 IR (liquid): 2929; 2854; 1704; 1458; 1374; 972.

H-NMR: (CDCl₃, 200 MHz); 5.35 (2H)m; 1.05
(3H)d; J = 6.5 Hz.

20 ¹³C-NMR: (CDCl₃) 215.75(s); 132.05(d); 130.34(d);
41.08 (t); 40.58 (d); 31.41 (t); 30.81
(t); 29.38 (t); 26.88 (t); 26.33 (t);
25.93 (t); 24.63 (t); 24.61 (t); 22.92
(t); 15.14 (q).

25 MS: 222 (100); 207 (4); 193 (41); 175 (17);
165 (31); 150 (46); 140 (34); 135 (24);
121 (40); 109 (61); 95 (77); 81 (85);
67 (94); 55 (89); 41 (77); 99 (15).

30

Fabric softener accord

Proportion by weight

E-3-Methylcyclotetradec-5-en-1-one (Example 3)	30
Phenylethyl acetate	30
35 Benzyl alcohol extra	100



	Hexylcinnamaldehyde	150
	Citronellol extra	50
	Coumarin	20
	Dynascone 10	1
5	Floralozon	4
	Isoraldein 70	100
	Lilial	250
	Linalool synt.	100
	Methylacetophenone	5
10	Methyl cedryl ketone	50
	Radjanol	10
	Amyl salicylate	50
	Terpineol	50
		<u>1000</u>

15

The compound prepared as in Example 3 gives volume and cleanliness to this floral, woody accord for a fabric softener. As a result of good substantivity, freshness and cleanliness are also retained on the dry laundry.

20 Fine fragrance accord

		Proportion by weight
	E-3-Methylcyclotetradec-5-en-1-one (Example 3)	50
	Benzyl acetate	15
	Ethyl acetoacetate	25
25	Ethyl phenyl alcohol	60
	Hexylcinnamaldehyde	70
	Ambrettolide	10
	Ambrofix	2
	Ethylene brassylate	100
30	Citronellol extra	50
	Cyclogalbonate	4
	Cyclohexal	20
	Ethyllinalool	80
	Oxyoctalin formate	15



	Gardenol	2
	Givescon	15
	Hedion	300
	Indole 10% PE	2
5	Isoraldein 95	35
	cis-Jasmone	3
	Lilial	80
	Methyl pamplemousse	20
	Black pepper ess.	10
10	Tricyclal	2
	Tropional	<u>30</u>
		1000

15 The compound prepared as in Example 3 gives this floral, transparent accord for alcoholic perfumes richness, a musk-like powdery effect which combines harmoniously with the floral, fruity part of the accord.

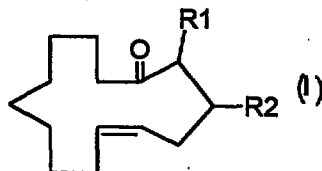
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Claims:

1. A compound of the formula I



5 in which R^1 and R^2 are hydrogen or methyl, with the proviso that, when R^1 is methyl, R^2 is hydrogen, and when R^1 is hydrogen, R^2 is methyl, it being possible
10 for the compounds of the formula I to be in the Z- and/or in the E-form.

2. E-3-Methylcyclotetradec-5-en-1-one.
- 15 3. Z-3-Methylcyclotetradec-5-en-1-one.
4. R-E-3-Methylcyclotetradec-5-en-1-one.
5. S-E-3-Methylcyclotetradec-5-en-1-one.
- 20 6. R-Z-3-Methylcyclotetradec-5-en-1-one.
7. S-Z-3-Methylcyclotetradec-5-en-1-one.
- 25 8. E-2-Methylcyclotetradec-5-en-1-one.
9. Z-2-Methylcyclotetradec-5-en-1-one.
10. A scent composition comprising at least one
30 compound as claimed in one of claims 1 to 9.

