

[54] **BICYCLIC COMPOUNDS AND PROCESSES FOR MAKING AND USING SAME**

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[21] Appl. No.: **411,789**

Related U.S. Application Data

[62] Division of Ser. No. 263,219, June 15, 1972, abandoned.

[52] **U.S. Cl.**..... **252/522; 260/348 C**

[51] **Int. Cl.²**..... **A61K 7/46**

[58] **Field of Search**..... **252/522; 260/348 C**

[56] **References Cited**

UNITED STATES PATENTS

2,809,996	10/1957	Stoll.....	252/522
2,912,462	11/1959	Goldstein et al.....	252/522
3,072,709	1/1963	Saucy.....	252/522
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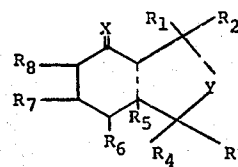
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[57] **ABSTRACT**

Bicyclic compounds containing four to six alkyl groups and having the formula:



wherein the dashed line is a single or double carbon-to-carbon bond; X is a carbonyl oxygen or two hydrogen atoms; Y is —CHR₉— or —CHR₁₀—CHR₁₁—; R₁, R₂, R₃ and R₄ are the same or different alkyl; R₇, R₈, R₉, R₁₀ and R₁₁ are hydrogen or the same or different alkyl, R₇ or R₈ being alkyl when R₉ is alkyl; R₅ is not present and R₆ is hydrogen when the dashed line is a double bond; and R₅ and R₆ are hydrogen, or taken together, form an oxirane ring when the dashed line is a single bond, together with methods of preparation for such bicyclic compounds, perfume compositions containing the compounds, and methods for altering aromas utilizing such compounds.

4 Claims, No Drawings

BICYCLIC COMPOUNDS AND PROCESSES FOR MAKING AND USING SAME

This is a division, of application Ser. No. 263,219, filed June 15, 1972 now abandoned.

BACKGROUND OF THE INVENTION

The present invention relates to polyalkyl bicyclic compounds, together with preparation of such compounds and their use for altering fragrances, and perfume compositions containing such bicyclic compounds.

There is a continuing need for fragrance materials having desirable woody odors with satisfactory olfactory overtones or qualities. Many natural products have such woody fragrances, but the more desirable of these are frequently in short supply, and hence difficult to obtain and expensive. Further, while both natural and synthetic materials can provide various woody fragrance qualities, many of these are fleeting and unsuitable for use in quality perfumes or other olfactory compositions. Moreover, it is desirable to have such fragrance materials with various overtones which can be blended with other materials.

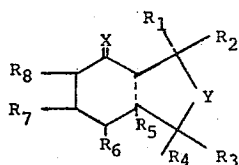
U.S. Pat. No. 3,265,739 shows a number of octalone materials which are stated to be useful for their fragrance properties. U.S. Pat. No. 3,636,165 shows hydrogenated indanols as having useful fragrances, and U.S. Pat. No. 3,647,826 shows epoxyperhydropentamethylindane as having a fine-pine-woody aroma. The use of perhydropentamethylindanone and of tetrahydropentamethylindane as fragrance compounds has also been suggested.

A pentamethyldecahydronaphthalen-7-one material called "Ketone BD-9" is sued for its wood, amber fragrance properties. Belgian Pat. No. 763,168 shows dialkyloctahydronaphthalenones and naphthalenols as perfume compounds. Tetraalkylperhydroindanone has also been suggested as having a musk, woody odor. *Tetrahedron Letters* 14, 627 shows indanone derivatives, as does *Helvetica Chimica Acta* 32(7), 2360. No aroma is suggested in these two journal articles, and similarly no odor is suggested for the naphthalenone derivatives shown in *J.A.C.S.* 85, 2014.

THE INVENTION

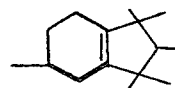
The present invention provides novel compounds which are suitable for a wide variety of perfume and other olfactory uses. Briefly, this invention contemplates bicyclic compounds containing at least four alkyl substituents on the ring and the rings of which comprise a 6-membered ring to which is fused either a 5-membered ring, or a 6-membered hydrocarbon ring. The invention also contemplates the use of such novel compounds, the use thereof to provide various pleasing aromas, perfume compositions containing the compounds; and various articles perfumed therewith.

More particularly, the bicyclic compounds contain from four to six alkyl groups substituent on the ring and respond to the formula:



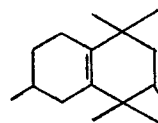
wherein the dashed line is a single or double carbon-to-carbon bond; X is carbonyl oxygen or two hydrogen atoms; Y is $-\text{CHR}_9-$ or $-\text{CHR}_{10}-\text{CHR}_{11}-$; R_1 , R_2 , R_3 , and R_4 are the same or different alkyl; R_7 , R_8 , R_9 , R_{10} , and R_{11} are hydrogen or the same or different alkyl, R_7 or R_8 being alkyl when R_9 is alkyl; R_5 is not present and R_6 is hydrogen when the dashed line is a double bond; and R_5 and R_6 are hydrogen or, taken together, form an oxirane ring when the dashed line is a single bond. The polyalkyl substituents are desirably lower alkyl groups, preferably those having from one to three carbon atoms in the group. The alkyl groups can be the same or different, and in certain preferred embodiments of the invention they are all methyl.

Thus, the preferred polyalkyl bicyclic compounds include a 4,5,6,7-tetrahydro-1,1,2,3,3,5-hexamethylindane, a liquid having the formula:



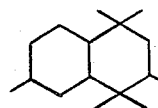
(I);

1,2,3,4,5,6,7,8-octahydro-1,1,3,4,4,6-hexamethylnaphthalene, a liquid having a boiling point of $111^\circ-112^\circ\text{C}$ at 2.0 mm Hg and the formula:



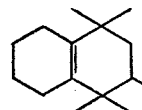
(II);

perhydro-1,1,3,4,4,6-hexamethylnaphthalene having the formula:



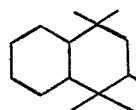
(III);

1,2,3,4,5,6,7,8-octahydro-1,1,3,4,4-pentamethylnaphthalene, a liquid boiling at $89^\circ-90^\circ\text{C}$ at 1.5 mm Hg and having the formula:



(IV);

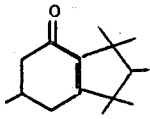
perhydro-1,1,3,4,4-pentamethylnaphthalene, having the formula:



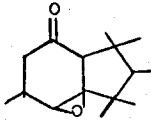
(v); and

4,5,6,7-tetrahydro-1,1,2,3,3,5-hexamethyl-7-indanone, having the formula:

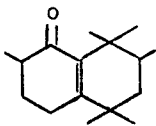
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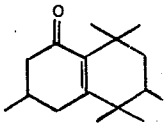
perhydro-1,1,2,3,3,5-hexamethyl-3a,4-epoxy-7-indanone, having the formula:



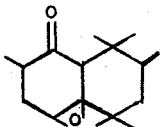
1,2,3,4,5,6,7,8-octahydro-1,1,2,4,4,7-hexamethyl-8-naphthalenone, having the formula:



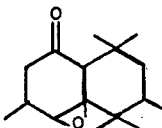
1,2,3,4,5,6,7,8-octahydro-1,1,3,4,4,6-hexamethyl-8-naphthalenone, having the formula:



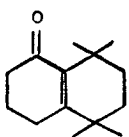
perhydro-1,1,2,4,4,7-hexamethyl-4a,5-epoxy-8-naphthalenone, having the formula:



perhydro-1,1,3,4,4,6-hexamethyl-4a,5-epoxy-8-naphthalenone, having the formula:

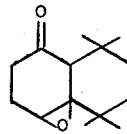


1,2,3,4,5,6,7,8-octahydro-1,1,4,4-tetramethyl-8-naphthalenone, having the formula:



perhydro-1,1,4,4-tetramethyl-4a,5-epoxy-8-naphthalenone, having the formula:

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(VI);

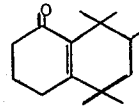
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(XIII);

1,2,3,4,5,6,7,8-octahydro-1,1,2,4,4-pentamethyl-8-naphthalenone, having the formula:

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(VII);



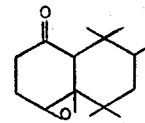
(XIV);

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perhydro-1,1,2,4,4-pentamethyl-4a,5-epoxy-8-naphthalenone, having the formula:

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(VIII);



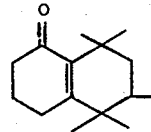
(XV);

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1,2,3,4,5,6,7,8-octahydro-1,1,3,4,4-pentamethyl-8-naphthalenone, having the formula:

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(IX);



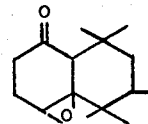
(XVI);

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perhydro-1,1,3,4,4-pentamethyl-4a,5-epoxy-8-naphthalenone, having the formula:

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(X);



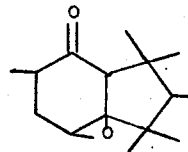
(XVII);

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perhydro-1,1,2,3,3,6-hexamethyl-3a,4-epoxy-7-indanone, having the formula:

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(XI);



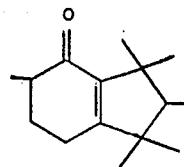
(XVIII); and

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4,5,6,7-tetrahydro-1,1,2,3,3,6-hexamethyl-7-indanone, having the formula:

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(XII);



(XIX).

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The novel oxygenated compounds of this invention have various fragrance notes. Thus, a mixture of com-

pounds VI, VII, XVIII, and XIX adds a fruity, amber, woody fragrance to perfumes. A mixture of XIV, XV, XVI, and XVII has a fruity, wood, peach aroma flavor character. A mixture of compounds VIII, IX, X, and XI has a warm ambergris aroma.

The novel compounds disclosed herein can be prepared from the corresponding indane or naphthalene hydrocarbons according to the methods herein disclosed. Thus, compound VI or VII can be prepared from hexamethyl indane; compound VIII or X, from hexamethyltetrahydronaphthalene; and similarly for other compounds.

One process for producing the novel compounds comprises treating the hydrocarbon having one aromatic ring with an alkali metal in the presence of ammonia or an amine. Lithium is the preferred alkali metal because the reaction rate is higher and better completeness is obtained. The alkali metal is desirably added in a form having a high surface area and pieces of the metallic ribbon have been used in certain preferred embodiments of the invention.

The amines used in conjunction with the alkali metal are desirably primary amines. The amines can be mono-amines having from two to five carbon atoms or diamines having from two to five carbon atoms. Ethylene diamine is an example of a primary amine preferred for use herein.

The amount of alkali metal used is in molar excess of the hydrocarbon being reduced, and amounts of from five to ten times the molar amount of hydrocarbon are preferred. The amount of nitrogen compound, e.g., diamines, used is generally sufficient to act as a vehicle for the reduction, so that it assists in moderating the reaction. Amounts of amine from three to 15 times the amount of hydrocarbon are desirably used. All parts, proportions, percentages, and ratios herein are by weight unless otherwise indicated.

When ammonia is utilized, the reaction is desirably carried out at temperatures of from about -50°C to about 0°C . Such temperatures obviate the substantial superatmospheric pressures which would result from higher temperatures, but a satisfactory reaction rate is still obtained.

When the amine compounds are utilized, their relatively lower vapor pressures enable the reaction to be carried out at temperatures of 80°C to 150°C to provide good completeness and to permit control of the course thereof. Times on the order of two to eight hours are desirably used at the preferred temperatures set forth herein.

Reduction of the aromatic ring, to provide monoenoic hydrocarbon, can also be carried out by high-pressure hydrogenation using a suitable catalyst. Hydrogen pressures of from 20 to 70 atmospheres are used at temperatures of 50°C to 200°C . The catalysts are desirably metal catalysts, and nickel, particularly Raney nickel, and rhodium-on-carbon are preferred.

After hydrogenation is completed, the catalyst is removed by filtration or other conventional techniques. The product is then purified as hereinafter disclosed.

The carbonyl oxygen-containing derivatives according to the present invention are prepared from monoenoic hydrocarbons obtained as taught herein. The monoenoic hydrocarbons are treated with an oxidizing agent. Alkali metal dichromates are desirably used and sodium dichromate ($\text{Na}_2\text{Cr}_2\text{O}_7$) is a preferred agent.

The oxidation reaction is desirably carried out in the presence of an acidic medium, generally an alkanolic acid and preferably a lower carboxylic acid having

from two to four carbon atoms. A preferred acidic medium is acetic acid.

The monoenoic hydrocarbon is generally utilized in molar excess of the dichromate to provide better reaction control. The molar quantity of dichromate is desirably about 80 percent to 95 percent of the molar quantity of the monoenoic hydrocarbon. The carboxylic acid is generally used in amounts of from about four times to about ten times the quantity of hydrocarbon.

The monoenoic or saturated hydrocarbons or the carbonyl derivatives produced according to the above reaction schemes can be separated from the reaction medium, and any unreacted materials or unwanted by-products removed by conventional means including washing, distillation, crystallization, extraction, preparative chromatography and the like. It is preferred fractionally to distill the washed reaction product under a relatively high vacuum so as to obtain a purified product or to isolate the pure material.

The monoenoic hydrocarbons according to the present invention are useful as intermediates in the preparation of fragrance materials, and are themselves useful as olfactory agents. The carbonyl compounds of this invention are useful as fragrances. They can be used singly or in combination to contribute woody, ambergris, and/or fruity fragrances. As olfactory agents the bicyclic derivatives of this invention can be formulated into or used as components of a "perfume composition".

The term "perfume composition" is used herein to mean a mixture of organic compounds, including, for example, alcohols, aldehydes, ketones, esters and frequently hydrocarbons which are admixed so that the combined odors of the individual components produce a pleasant or desired fragrance. Such perfume compositions usually contain: (a) the main note or the "bouquet" or foundation-stone of the composition; (b) modifiers which round-off and accompany the main note; (c) fixatives which include odorous substances which lend a particular note to the perfume throughout all stages of evaporation, and substances which retard evaporation; and (d) top-notes which are usually low-boiling fresh-smelling materials.

In perfume compositions the individual component will contribute its particular olfactory characteristics, but the overall effect of the perfume composition will be the sum of the effect of each ingredient. Thus, the individual compounds of this invention, or mixtures thereof, can be used to alter the aroma characteristics of a perfume composition, for example, by highlighting or moderating the olfactory reaction contribution by another ingredient in the composition.

The amount of the compounds of this invention which will be effective in perfume compositions depends on many factors, including the other ingredients, their amounts and the effects which are desired. It has been found that perfume compositions containing as little as one percent of compounds or mixtures of compounds of this invention, or even less, can be used to impart desirable aromas to soaps, cosmetics, and other products. The amount employed can range up to 15% or higher and will depend on considerations of cost, nature of the end product, the effect desired on the finished product and the particular fragrance sought.

The bicyclic derivatives of this invention can be used alone or in perfume compositions as olfactory components in detergents and soaps; space deodorants; perfumes; colognes; bath preparations such as bath oil, bath salts; hair preparations such as lacquers, brillian-tines, pomades, and shampoos; cosmetic preparations

such as creams, deodorants, hand lotions, sun screens; powders such as talcs, dusting powders, face powder, and the like. When used as an olfactory component of a perfumed article, as little as 0.011% of the novel bicyclics will suffice to impart a good woody odor.

In addition, the perfume composition can contain a vehicle or carrier for the other ingredients. The vehicle can be a liquid such as alcohol, glycol, or the like. The carrier can be an absorbent solid such as a gum or components for encapsulating the composition.

It will be appreciated that the bicyclic derivatives according to this invention can be used to enhance, modify, or supplement the fragrance properties of natural or synthetic fragrance compositions. Thus, such derivatives can be used in fragrance compositions for addition to perfume compositions or directly to products such as soap, detergents, cosmetics, and the like. The fragrance compositions so prepared do not entirely provide the olfactory properties to the finished perfume or other article, but they do furnish a substantial part of the overall fragrance impression.

The following examples are given to illustrate embodiments of the invention as it is presently preferred to practice it. It will be understood that these examples are illustrative, and the invention is not to be considered as restricted thereto except as indicated in the appended claims.

EXAMPLE I

A 12-liter, three-necked reaction flask is charged with 505 g (2.5 mole) of 1,1,2,3,3,5-hexamethylindane and 4700 cc ethylene diamine. The mixture is heated to 95°C, and 140 g (20 mole) of lithium ribbon is added slowly over four hours.

After the addition, the mixture is heated to reflux, so maintained for one hour, and cooled to 10°C. Six liters of water is added slowly with cooling over two hours, while maintaining the temperature below 50°C. The reaction mass is stirred for two hours and then separated.

The aqueous layer is extracted thrice with threeliter portions of toluene. The combined oil layers are washed consecutively with three liters each of water, 5% aqueous hydrochloric acid, and water. After stripping off solvent, the residue is fractionated, using a 12-inch Goodloe column to give 369 g of 4,5,6,7-tetrahydro-1,1,2,3,3,5-hexamethylindane (I).

EXAMPLE II

A one-gallon stirred autoclave is charged with 900 g of 1,1,3,4,4,6-hexamethyl-1,2,3,4-tetrahydronaphthalene, 900 cc isopropanol, and 45 g. of Raney nickel. Hydrogenation is conducted at 1500 psi and 175°-200°C to an uptake of two moles of hydrogen. The oil is freed of nickel catalyst by filtration and the solvent is stripped off. Gas-liquid chromatography (GLC) indicates the presence of approximately 20% 1,1,3,4,4,6-hexamethyl-1,2,3,4,5,6,7,8,9-octahydronaphthalenone (II) and 20% of 1,1,3,4,4,6-hexamethylperhydronaphthalene (III), with the remainder being the starting material.

EXAMPLE III

A 300 cc stirred autoclave is charged with 100 g (0.5 mole) of 1,1,2,4,4-pentamethyl-1,2,3,4-tetrahydronaphthalene and 5 g of 5% rhodium-on-carbon catalyst. Hydrogenation is conducted at 1000 psi and 70°C to an uptake of two moles of hydrogen.

The oil is freed of catalyst by filtration and GLC indicates the presence of 30% of compound IV and 40% of the completely saturated hydrocarbon V. The remainder is starting material.

EXAMPLE IV

A 5-liter reaction flask is charged with 366 g (1.73 mole) of 4,5,6,7-tetrahydro-1,1,2,3,3,5-hexamethylindane. A solution of 463 g (1.55 mole) of sodium dichromate in 1900 g of glacial acetic acid is added dropwise over one hour while maintaining the reaction mass at 75°C. After the addition is complete, stirring is continued at 75°C for another seven hours.

After cooling to room temperature, 1.5 liters of water is added and after stirring for 15 minutes, the layers are separated. The aqueous phase is extracted with one liter of toluene and the combined organic layers are washed with one liter each of water, 5% aqueous sodium hydroxide, and water.

The solvent is stripped off and the residue is fractionated to yield 141 g (50% yield) of a mixture of compounds VI and VII of molecular weight 220 and 236, respectively. The mixture also contains compounds XVIII and XIX.

EXAMPLE V

The procedure of Example IV is repeated utilizing compound II, and a 15% yield of the mixture of compounds VIII, IX, X, and XI is obtained. The liquid shows IR (infrared) absorption at 1665 and 1590 cm^{-1} attributed to conjugated carbonyl and absorption at 1710 cm^{-1} attributed to

EXAMPLE VI

The procedure of Example IV is repeated utilizing 1,2,3,4,5,6,7,8-octahydro-1,1,4,4-tetramethylnaphthalene, and a mixture of compounds XII and XIII is obtained in a 33% yield.

EXAMPLE VII

The following mixture is prepared:

4'-Butyl-2',6'-dimethyl-3',5'-dinitroacetophenone	100
Vanilla	75
Labdanum resin absolute	40
Patchouli oil	5
Cinnamic alcohol	10
Styrax clarified extra	10
Benzoin coeur	50
Mixture produced by the process of Example XII	50

The addition of the mixture produced by the process of Example XII imparts a warm ambergris character to this composition.

EXAMPLE VIII

The following mixture is prepared:

Lemon oil California	110
Bergamot oil Italian	150
Orange oil Florida	50
Neroli absolute	5
Petitgrain oil	75
Linalool synthetic	20
Linalyl acetate synthetic	50
Geranium bourbon oil	10
Rosemary oil	5
Benzoin coeur	10
Mixture produced by the process of Example IV	50

Addition of the mixture produced by the process of Example IV causes a fruity amber woody character to be imparted to this mixture.

EXAMPLE IX

The following mixture is prepared:

2-Heptylcyclopentanone	10
Benzyl salicylate	20
Phenylethyl alcohol coeur	100
4-(2,6,6-Trimethyl-2-cyclohexen-1-yl)-3-methyl-3-buten-2-one	25
Petitgrain oil	30
p-Isopropyl- α -methylhydrocinnamaldehyde	25
n-Decanal	1
Lauraldehyde	2
Methylnonyl acetaldehyde	0.5
Linalool synthetic	40
Linalyl acetate	50
Mixture produced by the process of Example V	50

The addition of the mixture produced by the process of Example V imparts a fruity woody peach note to the overall composition.

EXAMPLE X

A 22-liter flask fitted with a mechanical stirrer, thermometer, condenser, and addition funnel is charged with 1400 g of water, and 4900 g of sulfuric acid is rapidly added while the temperature is maintained at 30° to 40° with cooling. Then, 35 g of Triton X-100 octylphenoxypolyethoxyethanol surface active agent is added, and this is followed by the dropwise addition of a mixture of 3500g (29.4 moles) of alpha-methylstyrene and 1750 g (16.8 moles) of 2,3-dimethyl-2-hydroxybutane. The addition consumes 1-½ hours and the temperature is maintained at 30° to 35°C.

The addition of the mixture is exothermic, and cooling is required to maintain the temperature in the stated range. After addition is complete, the reaction mass is stirred for two hours at 30°-35°C; six liters of water is added; and the mixture is then heated to 95°C and stirred at that temperature for 30 minutes.

The reaction mass is left to stand for an additional 30 minutes after stirring has been completed, and an emulsion forms. The mixture is saturated with sodium chloride and four additional liters of water are added to cause separation of organic and aqueous layers. The aqueous layer is extracted thrice with three liters of toluene, the extract is combined with the organic phase, and the mass is washed with five liters of 5% aqueous sodium hydroxide and then with five liters of water. The solvent is stripped from the washed material, and the residue is vacuum distilled commencing at 6 mm Hg to provide 1113 g of product, a 33% yield.

The 1,1,2,4,4-pentamethyl-1,2,3,4-tetrahydronaphthalene so produced has a boiling point of 138°-142°C at 1.5 mm Hg.

EXAMPLE XI

A 12-liter flask equipped with stirrer, thermometer, condenser, and gas bubbler is charged with 490 g (2.2 moles) of pentamethyltetrahydronaphthalene produced in Example X and 4125 g of ethylene diamine and heated to 95°C, whereupon 123 g (17.6 moles) of pieces of lithium ribbon are added during 2-½ hours, while the temperature is maintained at 95° ± 5°C. The rate of lithium addition is determined by the evolution of gas. After all of the lithium is added the mass is heated to reflux and maintained under reflux for one

hour. During this time, the color of the reaction mass changes from blue to a creamy color.

The reaction mass is then cooled to 20°C and six liters of water is added dropwise with careful cooling to keep the highly exothermic reaction from raising the temperature above 60°C. During the initial addition of the water, the mass becomes very viscous, but further addition of water increases the fluidity and makes the mass easier to stir. After the water is added, the mass is stirred to dissolve all solids.

The stirring is discontinued to permit the formation of an aqueous layer and an organic layer and the aqueous layer is extracted once with two liters of toluene. The toluene extract is added to the organic layer and the mixture is washed successively with three liters of water, three liters of 5% aqueous hydrochloric acid, and three liters of water. The crude is stripped of solvent, and vacuum distilled at 2.5 - 1.7 mm Hg.

A 68.5% yield of 1,1,3,4,4-pentamethyl-1,2,3,4,5,6,7,8-octahydronaphthalene (IV) is obtained with a boiling point of 100°-109°C at 1.7 mm Hg.

EXAMPLE XII

A 5-liter reaction flask equipped with a stirrer, thermometer, condenser, and addition funnel is charged with 309 g (1.5 moles) of the product of Example XI and heated to 75°C, and a solution of 400 g sodium dichromate (1.35 moles) in 1650 cc of acetic acid is added dropwise during a one-hour period. The reaction mass is then stirred for eight hours.

The mixture is cooled to 25°C, 1.5 liters of water is added, the mixture is stirred for 10 minutes, and the aqueous and organic phases are then separated. The aqueous layer is extracted once with 500 cc of toluene, and the toluene extract is combined with the organic layer. The organic layer is then washed once successively with 500 cc of water, 500 cc of 5% aqueous sodium hydroxide, and 500 cc of water. The crude oil is stripped free of solvent and vacuum distilled at 2.8 mm Hg.

The product obtained in a 25% yield is a mixture of XIV, XV, XVI, and XVII, boiling at 142°-149°C at 2.8 mm Hg.

EXAMPLE XIII

A 12-liter reaction flask equipped with a stirrer, thermometer, condenser, and addition funnel is charged with 667 g of water, and 2335 g (23.8 moles) of sulfuric acid is added as rapidly as possible while maintaining the temperature at 30°-40°C. After 17 g of Triton X-100 surface active agent is added, a mixture of 1850 g (14 moles) p-methylalpha-methylstyrene and 816 g (8 moles) of 2,3-dimethyl-2-hydroxybutane is added dropwise at 30°-35°C with cooling during one hour. The mixture is then stirred for 1¼ hours at 30°-35°C with slight cooling required to maintain the temperature. Five liters of water is added, and the mixture is heated to 95°C and maintained at that temperature for 30 minutes. The stirring is discontinued, and the mixture is allowed to set for 30 minutes to separate into an aqueous phase and an organic phase. The aqueous layer is withdrawn and extracted with two liters of toluene, and the extract is combined with the organic layer. The combined organic layers are washed once with two liters of 5% aqueous sodium hydroxide and once with two liters of water and then stripped to free them of solvent. The stripped mixture is vacuum distilled at 2.5 mm Hg.

The 1,1,2,4,4,7-hexamethyl-1,2,3,4-tetrahydronaphthalene is obtained as a liquid boiling at 142°–155°C at 2.5 mm Hg in a yield of 55%.

EXAMPLE XIV

A 12-liter reaction flask equipped with stirrer, thermometer, and condenser is charged with 720 g (2 moles) of the tetrahydronaphthalene produced in Example XIII and 3750 cc of ethylene diamine. The flask contents are heated to 95°C and 113 g (16.0 moles) of metallic lithium ribbon is added in the form of small pieces during a 1½ hour period. The addition of lithium is exothermic and the flask is cooled to maintain the temperature at about 95°C, the rate of addition being controlled by observation of the amount of gas evolved. The color of the reaction mixture is blue so long as metallic lithium is present. Following the lithium addition, the reaction mass is refluxed for one hour.

The mass is then cooled to 10°C and six liters of water is added dropwise, with cooling required to maintain the exothermic water addition at a temperature below 40°C. When about one liter of water is added, the reaction mixture assumes a gelled consistency which liquifies on further addition of water. After the entire quantity of water is added, the reaction mass is stirred for three hours to dissolve all solid materials.

After the solids are dissolved, stirring is stopped and the reaction mass separates into aqueous and organic layers. The aqueous layer is extracted once with two liters of toluene, and the extract is combined with the organic layer. The combined extract and organic layer are then washed successively with three liters of water, three liters of 5% aqueous sodium hydroxide, and three liters of water. The solvent is then stripped off and the remaining material is subjected to vacuum distillation.

There is an 88% yield of 1,1,3,4,4,6-hexamethyl-1,2,3,4,5,6,7,8-octahydronaphthalene (II) mixed with about 10% of 1,1,3,4,4,6-hexamethylperhydronaphthalene. The mixture has a boiling point of 116°–124°C at 2.0 mm Hg.

EXAMPLE XV

A 5-liter reaction flask equipped with a stirrer, thermometer, condenser, and addition funnel is charged with 407 g (1.4 moles) of 76% hexamethyloctahydronaphthalene produced in Example XIV. The flask is then heated to 75°C and a mixture of 376 g (1.26 moles) of sodium dichromate and 1540 g of acetic acid is added dropwise during one hour while the temperature is maintained at 75°C. After addition of the sodium dichromate mixture is completed, the reaction mass is stirred for 7 hours at 75°C.

The mass is then cooled to 25°C and 1.5 liters of water is added. The mixture is stirred for 15 minutes and separated into two layers, and the aqueous phase is extracted once with one liter of toluene. The toluene extract and organic layer are combined and washed successively with one liter of water, one liter of 5% aqueous sodium hydroxide and one liter of water. The solvent is stripped from the washed product and vacuum distilled.

A liquid mixture of XIV, XV, XVI, and XVII, boiling at 112°–124°C under 2 mm Hg is obtained. The yield of the mixture products is about 30%. IR spectroscopy shows absorption at 1665 and 1590 cm⁻¹ attributed to conjugated carbonyl groups and absorption at 1710 cm⁻¹ attributed to unconjugated carbonyl groups.

EXAMPLE XVI

A 12-liter reaction flask is equipped with stirrer, thermometer, condenser, and addition funnel is charged with 475 g of water and 1665 g of concentrated sulfuric acid is added with cooling to maintain the temperature in the range of 30°–40°C. Twelve grams of Triton X-100 is added, and this is followed by the dropwise addition of a mixture of 1320 g (10 moles) of p-methyl-alpha-methylstyrene and 510 grams (5.8 moles) of t-amyl alcohol, with the temperature being maintained at 30°–35°C. The addition takes one hour and the mixture is thereafter stirred at 30°–35°C for 1½ hours. Thereafter, three liters of water is added, and the mixture is heated to 95°C, and the temperature is maintained at 35°C for 30 minutes.

The mixture is allowed to set for 30 minutes and is then separated into an aqueous and organic layer. The aqueous layer is extracted with two liters of toluene and combined with the organic layer, and the combination is washed successively with two liters of 5% aqueous sodium hydroxide and two liters of water. The crude product is stripped to remove the solvent and vacuum distilled.

A 59% yield of liquid 1,1,2,3,3,5-hexamethylindane boiling at 116°–140°C at 2.5 mm Hg is obtained.

EXAMPLE XVII

A 12-liter reaction flask equipped with stirrer, thermometer, condenser, and gas bubbler is charged with 505 g (2.5 moles) of the indane produced in Example XVI and 4700 cc of ethylene diamine. The mixture is heated to 95°C and 140 g (20 moles) of lithium ribbon is added in the form of pieces during four hours. When all of the lithium has reacted, the color of the reaction mass changes from blue to yellow, and no additional gas is evolved. The rate of addition of lithium is controlled by adding further lithium when gas evolution from the previous addition has stopped. After lithium addition is complete, the mass is heated to reflux and maintained for one hour.

The mass is cooled to 10°C and six liters of water is added dropwise with cooling to maintain the exothermic reaction below 50°C. During water addition, the reaction mass gels, but upon further addition of water, the solids dissolve. The water addition takes about two hours, and then the mass is stirred for an additional two hours and permitted to separate into two phases.

The aqueous phase is extracted with three liters of toluene and combined with the organic phase and the combination is washed successively with three liters of water, three liters of 5% aqueous hydrochloric acid and three liters of water. The solvent is stripped off and the product is vacuum distilled.

1,1,2,3,3,5-Hexamethyl-4,5,6,7-tetrahydroindane (I) is obtained in a 75.8% yield as a liquid boiling at 92°–95°C at 3 mm Hg.

EXAMPLE XIII

A 5-liter reaction flask equipped with stirrer, thermometer, condenser, and addition funnel is charged with 366 g (1.73 moles) of 97.2% pure pentamethylindane produced in Example XVII. The flask is heated to 75°C and a mixture of 463 g (1.55 moles) of sodium dichromate and 1900 g of acetic acid is added dropwise during one hour. After the addition is complete, the mass is stirred for seven additional hours at 75°C.

The mass is cooled to 25°C, 1.5 liters of water is added, and the mixture is stirred for 15 minutes. The aqueous and organic phases are separated and the aqueous phase is extracted with a liter of toluene. The toluene extract is combined with the organic layer, and the combination is washed successively with a liter of water, a liter of 5% aqueous sodium hydroxide, and a liter of water. The solvent is stripped from the mixture, and the mixture is then vacuum distilled.

A mixture of VI, VII, XVIII, XIX is obtained as a liquid boiling at 110°–116°C at 2 mm Hg in a yield of 48%. Infrared (IR) spectroscopy shows absorption at 1665 and 1625 cm⁻¹ attributable to conjugated carbonyl groups and absorption at 1710 cm⁻¹ attributable to unconjugated carbonyl groups.

EXAMPLE XIX

A high-pressure autoclave is charged with 900 g 1,1,3,4,4,6-hexamethyl-1,2,3,4-tetrahydronaphthalene, 900 cc of isopropanol, and 45 g of Raney nickel catalyst. The hydrogenation reaction is started at 50°C and 300 psig (pounds per square inch, gauge) pressure, and over a four-hour time the temperature is raised to 200°C and the pressure to 1200 psig.

After the foregoing hydrogenation is completed, the catalyst is filtered off and the solvent is stripped from the reaction mixture. Mass spectroscopic analysis of the product shows it contains 20% 1,1,3,4,4,6-hexamethyl-1,2,3,4,5,6,7,8-octahydronaphthalene (II) and 20% 1,2,3,4,5,6-hexamethylperhydronaphthalene.

EXAMPLE XX

A high-pressure autoclave is charged with 200 cc of 1,1,3,4,4,6-hexamethyl-1,2,3,4-tetrahydronaphthalene and 5 g of 5% rhodium-on-carbon catalyst. The hydrogenation is commenced at 32°C and 280 psig, and the temperature and pressure are, respectively, raised to 175°C and 1500 psig during 2.5 hours. An additional 5 g of the aforesaid catalyst is then added, and the hydrogenation is continued at 100°–155°C and 1500 psig for another hour.

After the foregoing hydrogenation is completed the catalyst is filtered off. Gas-liquid chromatography (GLC) shows that the 86 g of product is obtained is 1,1,3,4,4,6-hexamethyl-1,2,3,4,5,6,7,8-octahydronaphthalene.

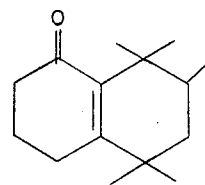
EXAMPLE XXI

A high-pressure autoclave is charged with 101 g (0.5 moles) of 1,1,2,4,4-pentamethyl-1,2,3,4-tetrahydronaphthalene and 5 g of 5% rhodium-on-carbon catalyst. The hydrogenation is begun at 25°C and 1000 psig pressure, and after about an hour the temperature is gradually raised to 70°–75°C, and the reaction is completed in about 2 hours and 20 minutes.

After the material is removed from the autoclave the catalyst is separated by filtration. GLC analysis shows that 30 percent of the material is 1,1,2,4,4-pentamethyl-1,2,3,4,5,6,7,8-octahydronaphthalene and that 40 percent is 1,1,2,4,4-pentamethyl-1,2,3,4,5,6-hexahydronaphthalene. Mass spectroscopy confirms these results.

What is claimed is:

1. A perfume composition containing as an essential fragrance ingredient 1,2,3,4,5,6,7,8-octahydro-1,1,2,4,4-pentamethyl-8-naphthalenone having the formula



and an auxiliary perfume adjuvant selected from the group consisting of perfume modifiers, fixatives and top-notes.

2. A composition as defined in claim 1 which additionally comprises 1,2,3,4,5,6,7,8-octahydro-1,1,3,4,4-pentamethyl-8-naphthalenone; perhydro-1,1,2,4,4-pentamethyl-4a,5-epoxy-8-naphthalenone; and perhydro-1,1,3,4,4-pentamethyl-4a,5-epoxy-8-naphthalenone.

3. A process for altering the fragrance properties of a perfumed composition which comprises adding at least about 0.011 per cent by weight based on the weight of said composition of 1,2,3,4,5,6,7,8-octahydro-1,1,2,4,4-pentamethyl-8-naphthalenone thereto.

4. A process as defined in claim 3, wherein said composition additionally contains 1,2,3,4,5,6,7,8-octahydro-1,1,3,4,4-pentamethyl-8-naphthalenone; perhydro-1,1,2,4,4-pentamethyl-4a,5-epoxy-8-naphthalenone; and perhydro-1,1,3,4,4-pentamethyl-4a,5-epoxy-8-naphthalenone.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 3,927,083

DATED : December 16, 1975

INVENTOR(S) : JOHN B. HALL, LEKHU KEWALRAM LALA,
MUUS G. J. BEETS, and WILLIAM I. TAYLOR

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Col. 1, line 36, "sued" should read --used--

Col. 8, line 33, complete the sentence and insert
after "to" --unconjugated carbonyl--

Col. 8, Example VII, insert "-t-" after "4'"

Col. 9, line 32, at the end of the line "methylysy-"
should read --methylsty--

Signed and Sealed this

Twenty-seventh Day of July 1976

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks