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3,028,431

PROCESS FOR PREPARING ORGANOLEPTIC MATERIALS

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This invention is concerned with producing hydroxy dihydrocitronellal, citronellal, citronellol and other related valuable terpene compounds from 7,8-epoxy-2,6-dimethyl-octane-2-ol.

It is well known that certain naturally-occurring, but imported, essential oils, such as oil of citronella, are highly prized for their content of citronellal and citronellol, which compounds are not only valuable as constituents of flavor and perfume compositions, but are also valuable as intermediates for synthesis of many other compounds useful as flavors and perfumes. Thus, citronellal is converted to menthol and hydroxycitronellal. Citronellol is esterified with the lower carboxylic acids to produce esters valuable in formulating perfumery products.

Since the price, quality and availability of such important and highly valued imported oils fluctuates widely, it is very desirable to provide a process by which readily available and inexpensive domestic terpenes can be converted to the most important ingredients of these oils, citronellal and citronellol and their derivatives.

Alpha- and beta-pinenes are readily available from domestic turpentine and can be hydrogenated to pinane. Pinane yields 2,6-dimethyl-2,7-octadiene or pyrolysis; Pines, J.A.C.S., 76, 4412 (1954). This acyclic diene can be converted to 2,6-dimethyl-7-octene-2-yl compounds according to the methods described in Serial No. 576,795, filed April 9, 1956, now U.S. Patent No. 2,902,510. These 2,6-dimethyl-7-octene-2-yl compounds can be converted to 7,8-epoxy-2,6-dimethyl-octan-2-yl compounds by methods described in Serial No. 576,794, filed April 9, 1956, now U.S. Patent No. 2,902,495.

It is accordingly an object of the present invention to provide a method for making oxygenated terpenes.

Another object is to provide a method for producing citronellal, hydroxycitronellal, citronellol, hydroxycitronellol, isomers thereof and esters and ethers of the alcohols.

A further object is to provide a method for converting certain alcohol derivatives of 2,6-dimethyl-octane to the corresponding carbonyl analogues.

An additional object is to convert citronellol and hydroxycitronellol into the corresponding aldehyde.

Still another object is to convert 7,8-epoxy-2,6-dimethyl-octane-2-ol into hydroxycitronellol and citronellol.

I have now found that 7,8-epoxy-2,6-dimethyl-octan-2-ol can be hydrogenated to produce 2,6-dimethyl-octane-2,8-diol, which can be dehydrogenated to produce hydroxy dihydrocitronellal, commonly referred to as hydroxycitronellal, or alternatively it can be selectively dehydrated to produce citronellol, 2,6-dimethyl-2-octen-8-ol, which, in turn, can be dehydrogenated to produce citronellal. It is a particularly valuable aspect of my invention that if optically active pinenes are employed as raw materials for preparation of the 7,8-epoxy-2,6-dimethyl-octane-2-ol, then the products produced accord-

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ing to the present invention will also be optically active. Thus, if I employ levo rotatory pinenes as raw materials, the acyclic compounds produced, citronellal, citronellol and hydroxycitronellal, will all be dextro rotatory and will be about as optically pure as the original pinene since little racemization takes place throughout the series of reactions involved.

In hydrogenating the 7,8-epoxy-2,6-dimethyl-octane-2-ol, I find that reduction with sodium in isopropanol can be employed, but in addition to the primary alcohol, a part of the reduced product is 2,6-dimethyl-7-octene-2-ol which results from de-epoxidation. Another product is 2,6-dimethyl-octane-2,7-diol which is of value for synthesis of acyclics oxygenated at the 7-position, and the 2,7-diol itself has value as a fixative in perfumery and as a mosquito repellant.

I find that catalytic hydrogenation of the epoxide is preferable to sodium reduction for production of citronellol, hydroxycitronellol and their aldehyde analogues. Here, an undesirable side reaction is de-epoxidation and reduction of the de-epoxidized product to 2,6-dimethyl-octane-2-ol. The hydrogenation of the oxirane ring can take place at either side of the oxygen atom so that either the 2,7-diol or the 2,8-diol can be formed. In practice, both of these diols are produced, though in widely varying proportions depending upon hydrogenation conditions, particularly upon the identity of the catalyst employed. Thus, we prefer to employ cobalt or nickel catalysts, suitably of the Raney type, to secure highest conversions to the 2,8-diol. Other hydrogenation catalysts including copper chromite, palladium, etc., can be employed, but result in production of larger proportions of the less widely useful 2,7-diol.

Hydrogen pressures are not critical though pressures of 500 to 1000 p.s.i.g. are economic to attain and are satisfactory as to rate of hydrogenation. The temperature of hydrogenation is not very critical, but temperatures of 100° to 175° C. have been found satisfactory with cobalt and nickel catalysts, while palladium can be used at ambient temperatures. The 7,8-epoxy-2,6-dimethyl-octan-2-ol is relatively viscous, and it is possible to increase the rate of hydrogenation through use of an inert solvent such as methanol and at the same time achieve higher yields of the desired 2,8-diol. When the hydrogenation is complete, the product can be fractionated, if desired, by distillation, preferably at reduced pressure, to obtain pure fractions of the 2,7-diol and the 2,8-diol.

The 2,6-dimethyl-octan-2,8-diol can be selectively dehydrated by boiling with relatively strong aqueous acids. Such treatment results in removal of the tertiary hydroxyl group with formation of unsaturation involving the number 2 carbon atom. If the dehydration is accomplished under conditions that favor the removal of the monohydric alcohol from the dehydrating reagent as it is produced, it will be rich in 2,6-dimethyl-1-octene-8-ol, α -citronellol, but if this dehydration product is permitted to remain in contact with the acid for some time, then isomerization of the double bond from the 1-position to the 2-position occurs and the final product of the dehydration-isomerization is β -citronellol, the predominate form found in natural oils. The identity of the mineral acid is not critical, that is, sulfuric or oxalic can be employed but phosphoric acid is satisfactory, cheap and is a relatively non-corrosive acid which is quite satisfactory.

The phosphoric acid concentration is not critical, but we prefer to employ about 15 to 35% concentrations, since use of more dilute acid causes a drop in the rate of dehydration and more concentrated acids may cause ether and polymer formation.

Temperatures required for dehydration are not critical, but it is convenient to employ the temperature corresponding to refluxing at atmospheric pressure of the particular acid and concentration of choice. This will ordinarily involve temperatures of 100° to 130° C. Those skilled in the art will appreciate that superatmospheric pressures, higher temperatures, and weaker or more dilute acids could be used, but that such conditions would be less economic to achieve and would result in little or no change in yield of product since use of the simple preferred conditions results in almost quantitative yields.

Simple acid dehydration can be conducted as shown in Example 8 to obtain citronellol rich in the alpha form, whereas Example 3 provides details for production of citronellol almost exclusively in the beta form.

An alternate method for dehydration of the 2,8-diol and one capable of giving very high yields of the alpha form of citronellol is described in Example 9. Thus, if the lower carboxylic acid ester of alpha-citronellol is desired, it is convenient to reflux the acid anhydride with the 2,8-diol whereby the tertiary hydroxyl is lost with formation of a double bond at the 1-2 position, and the primary hydroxyl group at the 8-position is esterified. High yields of alpha-citronellol esters are so produced and are valuable as ingredients of perfume compositions. To obtain pure alpha-citronellol, it is necessary only to saponify such esters and purify the alcohol by distillation. An alternate to this procedure is to esterify the 2,8-diol with an anhydride such as acetic anhydride at lower temperatures, say, room temperature and in the presence of a catalyst such as phosphoric acid to produce the diester of the 2,8-diol. The diester can be purified by conventional methods or can simply be heated to reflux whereby the elements of acetic or other acid is lost from the tertiary position, but the primary ester linkage is stable. This selective pyrolysis of the diester takes place readily at 150° to 225° C. and the operation can be conducted under a fractionating column so that the carboxylic acid and the mono ester are removed as formed by pyrolysis.

The same considerations apply to treatments of the 2,7-diol to produce 2,6-dimethyl-1-octene-7-ol and 2,6-dimethyl-2-octene-7-ol and their esters. These products do not have well known commercial and established uses, as they do not occur in the common essential oils, but these alcohols and their lower monocarboxylic esters do have pleasant characteristic floral odors rendering them useful in aromatic compositions for perfumery including masking agents. The higher esters, including the esters of phthalic and azelaic acids, have little or no odor value but are valuable as fixatives and plasticizers for cellulose esters and for vinyl resins.

It is evident from the foregoing that the tertiary hydroxyl group of both the 2,7-diol and the 2,8-diol is readily removed to yield at will the alpha or beta forms of the corresponding secondary and primary monohydric alcohols. It is also evident that one can choose to produce either the dextro or levo optical forms of these through choice of the appropriate optical forms of pinane.

Certain analogs or derivatives of 7,8-epoxy-2,6-dimethyl-octane-2-ol can also be employed in the practice of certain aspects of my present invention. These equivalents are those 7,8-epoxy-2,6-dimethyl-octane-2-yl compounds which can be readily hydrogenated to the corresponding 2,6-dimethyl-octane-8-ol-2-yl compounds and include the lower alkyl ethers and esters of 7,8-epoxy-2,6-dimethyl-octane-2-ol which can be produced by the methods disclosed in copending application Serial No. 576,794.

Thus, 7,8-epoxy-2,6-dimethyl-octane-2-yl acetate can

be hydrogenated to produce a mixture of 2,6-dimethyl-octane-8-ol-2-yl acetate, and 2,6-dimethyl-octane-7-ol-2-yl acetate. These can be saponified readily to the glycols which are then further processed to citronellol, citronellal and hydroxycitronellal. The glycol mono esters can also be dehydrogenated with copper chromite as described herein, although some splitting of acetic acid from the 2-position may take place whereby a mixture of citronellal and 2-acetoxy-dihydrocitronellal is produced. The mono esters can also be treated with phosphoric acid as disclosed herein, whereby acetic acid is split out at the 2-position, thus producing alpha- and beta-citronellol.

Likewise, for example, 2-methoxy-7,8-epoxy-2,6-dimethyl-octane yields on hydrogenation, as described herein, a mixture of 2-methoxy-2,6-dimethyl-octane-7-ol and 2-methoxy-2,6-dimethyl-octane-8-ol. On treatment with boiling 25% phosphoric acid, these mono ethers yield methanol and the corresponding unsaturated secondary and primary alcohols, respectively, and rich or poor in unsaturation at the 1-position depending on duration of the acid treatment. Also, the 2-methoxy-2,6-dimethyl-octane-8-ol will yield 2-methoxy-2,6-dimethyl-octane-8-al on dehydrogenation with copper chromite. Some methanol may be split out during the dehydrogenation so that more or less citronellal will also be produced.

Several methods can be employed to convert the primary alcohols, 2,6-dimethyl-octane-2,8-diol and the two forms of citronellol to the corresponding aldehydes, hydroxy-dihydrocitronellal, alpha-citronellal and beta-citronellal. It is preferred to employ catalytic dehydrogenation methods for this purpose, in either vapor or liquid phase. In the use of vapor phase methods, it is necessary to vaporize the alcohol, suitably in a stream of inert gas such as nitrogen, and pass the vapors over a suitable catalyst such as a copper bearing catalyst, suitably a supported copper chromite, heated to temperatures in the range of 250 to 550° C. and at such a rate that substantial dehydrogenation takes place. The condensed vapors are then fractionated, preferably at reduced pressures, to separate unchanged alcohol and purified aldehyde.

It is satisfactory, however, to employ liquid phase dehydrogenation whereby the alcohol and a copper bearing catalyst are mixed and heated to cause dehydrogenation while the dehydrogenation products, aldehyde and hydrogen, are being removed by distillation substantially at the rate at which they are being formed so that the aldehyde is not subjected to long contact with hot catalyst.

Suitable dehydrogenation catalysts are copper chromite, copper powder, cuprous oxide, cupric oxide and, in general, those copper compounds which yield copper readily on heating in the presence of organic material such as copper basic carbonate, etc. Other catalysts such as nickel and cobalt can also be used, but to no particular advantage, and in the case of citronellol these cause not only formation of aldehyde but also cause some hydrogenation of the double bond involving the number two carbon atom to produce 2,6-dimethyl-octane-8-al, dihydrocitronellal. The copper bearing catalyst can be of mixed type, such as results from mixing solutions of copper, manganese, silver, etc., and adding a precipitant such as an alkali or alkali earth hydroxide or carbonate. The behavior of such catalysts with respect to causing dehydrogenation is similar and offers no great advantage over copper chromite and copper, which are cheap, commercially available and do not cause hydrogenation of the double bond if one is present at the 2-position.

In conducting the liquid phase dehydrogenation in the preferred manner, the 2,6-dimethyl-octane-2,8-diol or the citronellol is placed in a vessel preferably equipped with an agitator and a fractionating column for operation at reduced pressure. A suitable vacuum is applied so that the aldehyde and hydrogen are removed from contact with the catalyst as they are formed and so that the temperature in the vessel is such that a suitable reaction rate is maintained. In dehydrogenating the citronelloles,

a vacuum of 10 mm. absolute at the condenser caused the citronellol-catalyst mixture in the pot to boil at about 110–115° C., but at this temperature dehydrogenation was uneconomically slow. At a pressure at the condenser of 250 mm., the dehydrogenation was quite rapid, but the citronellal could not be removed from the reacting mixture fast enough and substantial decomposition of the aldehyde occurred due to long contact with catalyst. At 100 mm. vacuum, however, the reaction temperature in the stillpot was around 165° C., and citronellal and hydrogen could readily be removed through the fractionating column and at about the rate at which they were formed, so that the concentration of citronellal in the reacting mixture was only about 3 to 5%. Thus, the vapors leaving the pot were rich in citronellol, but the alcohol was returned to the stillpot as reflux and the aldehyde was removed at the head of the fractionating equipment as, say, 90% or higher purity aldehyde. Optimum temperatures and pressures may vary somewhat due to catalyst concentration, catalyst activity, efficiency and size of the fractionating column, etc., but can be readily determined for any specific set of conditions.

Similarly, in dehydrogenating the 2,6-dimethyl-octane-2,8-diol to produce hydroxy-citronellal, a pressure of 1 mm. at the head of the column does not provide a sufficiently high dehydrogenating temperature for the boiling liquid in the pot to be economic and 100 mm. provides such a high pot temperature that some degradation of the aldehyde to polymer may take place. At 10 mm. absolute pressure at the head of the column, smooth dehydrogenation took place at an economic rate and high quality aldehyde in high yield was collected from the top of the column. It will be understood that the apparent boiling point of the aldehyde being collected from a dehydrogenating mixture is below the true boiling point to the extent that the hydrogen being evolved lowers the aldehyde boiling point.

In general, 3 to 10% catalyst is found satisfactory, though the dehydrogenation mixture should be heated to a higher temperature with 3% than with 10% catalyst to secure comparable dehydrogenation rates. Smaller quantities of catalyst can be used, but usually with some sacrifice in yield of aldehyde because of the higher temperature and longer time required.

If desired, the dehydrogenation vessel can be fed continuously with catalyst and primary alcohol with only occasional shutdowns to remove spent catalyst and the traces of polymeric materials formed.

Refractionation of the crude aldehydes yields products of high purity and excellent organoleptic quality.

The secondary alcohols, 2,6-dimethyl-octane-2,7-diol and 2,6-dimethyl-(1 or 2)-octene-7-ols can be similarly dehydrogenated to the corresponding 2,6-dimethyl-octane-2-ol-7-one and 2,6-dimethyl-(1 or 2)-octene-7-ones and to the extent to which these secondary alcohols may be present in the primary alcohol fractions subjected to dehydrogenation, the ketones will also be produced and appear as impurities in the crude aldehyde. Thus, the crude mixture resulting from hydrogenation can be dehydrated and dehydrogenated and the purified products can be isolated by fractional distillation or by other means such as bisulfite formation in the case of the aldehydes.

While the 2-acyloxy- and 2-alkoxy-7,8-epoxy-2,6-dimethyl octanes can be so processed to obtain results analogous to those reported herein for the 2-hydroxy compound, I ordinarily prefer to employ the latter. Certain other 7,8-epoxy-2,6-dimethyl-octane-2-yl compounds are not well suited to analogous conversions, however. Thus, the chloride and bromide are not readily hydrogenated.

The optical rotations shown in the examples are those obtained by converting optically pure 1-pinane to 7,8-epoxy-2,6-dimethyl-octane-2-ol according to copending applications Serial Nos. 576,794 and 576,795, and

using this epoxide as raw material for hydrogenation and further processing. The epoxide, B.P. 121° C. at 10 mm., D_4^{25} 0.9531, N_D^{25} 1.4476, is slightly dextro rotatory when prepared from pure 1-pinane and shows α_D^{25} +0.95 (10 cm. tube).

It is to be noted that all compounds described here have been named as derivatives of 2,6-dimethyl-octane irrespective of the nature and location of functional groups in order to maintain consistent nomenclature for ease of reading this disclosure.

The following examples are illustrative:

EXAMPLE 1

One thousand grams of 7,8-epoxy-2,6-dimethyl-octane-2-ol was hydrogenated in the presence of 50 grams of Raney nickel catalyst and 300 ml. of methanol at 100–130° C. under a hydrogen pressure of 500–1000 p.s.i.g. and until absorption of hydrogen had about ceased. The amount of hydrogen absorbed amounted to about 1.05 moles per mole of epoxide. The hydrogenation product was filtered to remove catalyst and was fractionated by distillation. Infrared spectro-analysis of the fractions indicated that the hydrogenation product was 2–4% 2,6-dimethyl-octane-2-ol, B.P.₁₀ mm. 84.5° C., D_4^{25} 0.824, N_D^{25} 1.4311; 2–4% unchanged 7,8-epoxy-2,6-dimethyl-octane-2-ol; 14% 2,6-dimethyl-octane-2,7-diol, B.P.₁₀ mm. 137° C., D_4^{25} 0.924, N_D^{25} 1.4558, α_D^{25} (10 cm. tube) +11.83°; and 80% 2,6-dimethyl-octane-2,8-diol, hydroxy-dihydrocitronellol, B.P.₁₀ mm. 148° C., D_4^{25} 0.928, N_D^{25} 1.4578, α_D^{25} (10 cm. tube) +2.10°.

Identification of Compounds

The fraction boiling at 84.5° C. at 10 mm. had an infrared spectrum identical with the spectrum of a known sample of 2,6-dimethyl-octane-2-ol.

Infrared spectroanalysis of the fraction boiling at 137° C. at 10 mm. showed it was a diol, as indicated by the intensity of the hydroxyl absorption at about 3 μ . The diol contained a secondary and a tertiary hydroxyl group as shown by the presence of the characteristic secondary and tertiary hydroxyl absorptions at 9.15 μ and 8.8 μ , respectively. Dehydration of the diol by refluxing it with a 25% aqueous H_3PO_4 solution gave an unsaturated secondary alcohol, B.P.₁₀ mm. 97° C., D_4^{25} 0.859, N_D^{25} 1.4540, α_D^{25} (10 cm. tube) +10.4°, which dehydrated in the presence of a trace of iodine at 150–160° C. to 2,6-dimethyl-2,7-octadiene as determined by comparing the spectrum of the hydrocarbon with the spectrum of a known sample of 2,6-dimethyl-2,7-octadiene. From the above data it is evident that the fraction boiling at 137° C. at 10 mm. is 2,6-dimethyl-octane-2,7-diol, and that the unsaturated secondary alcohol of B.P. 97° C. at 10 mm. is 2,6-dimethyl-2-octene-7-ol.

Infrared spectroanalysis of the fraction boiling at 148° C. at 10 mm. showed that it was a diol, as indicated by the intensity of the characteristic hydroxyl absorption at about 3.0 μ . The diol contained a primary and a tertiary hydroxyl group, as shown by the presence of the characteristic primary and tertiary hydroxyl absorptions in the infrared spectrum at 9.5 μ and 8.8 μ , respectively. Dehydration of the diol by refluxing it with a 25% aqueous H_3PO_4 solution gave an oil which was identified as citronellol (93–95%) by comparing its infrared spectrum and physical properties with a known sample of natural citronellol. From the above data it is evident that the fraction boiling at 148° C. at 10 mm. is 2,6-dimethyl-octane-2,8-diol, hydroxy-dihydrocitronellol.

EXAMPLE 2

Two-hundred gram portions of 7,8-epoxy-2,6-dimethyl-octane-2-ol were hydrogenated using 1% of the catalysts and the solvents and conditions listed in Table I. The hydrogenation products were filtered and fractionated. The fractions were analyzed by infrared spectroanalysis.

TABLE I

Catalyst	Solvent	Hydrogen, p.s.i.g.	Temp., ° C.	Analysis of Product (% by weight)			
				Dimethyl- Octane- 2-ol	Unchanged Epoxide	2, 7-diol	2, 8-diol
Raney Cobalt.....	CH ₃ OH.....	500-1,000	100-130	2-4	1-2	10	85
Copper Chromite.....	CH ₃ OH.....	500-1,000	100-130	30	12	40	18
5.0% Pd on C.....	CH ₃ COOH.....	40-60	20-40	2	8	80	10
Raney Nickel.....	CH ₃ OH.....	500-1,000	100-130	3	4	35	58
Raney Nickel.....	None.....	500-1,600	150-170	6	2	16	76

¹ 1.0 gram NaOH added.

EXAMPLE 3

Two hundred grams of 2,6-dimethyl-octane-2,8-diol and 100 grams of an aqueous 25% H₃PO₄ solution were stirred at reflux, 100-105° C., for 1 hour, and the resulting oils were then removed by cohobation. One hundred and seventy-four grams of oil was obtained. Fractionation of the oil, followed by infrared spectroanalysis of the fractions, indicated that the oil was 93-95% citronellol. The pure citronellol obtained from the fractionation had the following properties: B.P.₁₀ mm., 107° C., N_D²⁵ 1.4543, D₄²⁵ 0.867, α_D²⁵ (10 cm. tube) +4.5°. This product was almost exclusively the beta form of citronellol.

EXAMPLE 4

Two hundred grams of β-citronellol, prepared as shown in Example 3, and 10 grams of copper chromite (Harshaw's CU-1106-P) were placed in the stillpot of an efficient fractionating column. The distillate was taken off at 100 mm. at such a rate that the head temperature stayed between 138 and 140° C. The reaction was completed in 12 to 16 hours. One hundred ninety grams of distillate was recovered. The distillate was 95-97% β-citronellal and 3-5% β-citronellol as determined by comparing its physical properties, B.P.₁₀₀ mm. 138-140° C., D₄²⁵ 0.851, N_D²⁵ 1.4450, α_D²⁵ (10 cm. tube) +9.87, and infrared spectrum with those of known β-citronellal and β-citronellol samples obtained from natural oils.

EXAMPLE 5

Two hundred grams of β-citronellol, prepared as shown in Example 3, and 10 grams of powdered copper were heated in the stillpot of a fractionating column as shown in Example 4. After 40 hours, 140 grams of distillate had been collected. Infrared spectroanalysis of the distillate showed that it was 90-95% β-citronellal and 5-10% β-citronellol. Infrared spectroanalysis of the oil remaining in the stillpot showed that it was 95-98% β-citronellol and 2-5% β-citronellal.

EXAMPLE 6

Two hundred grams of 2,6-dimethyl-octane-2,8-diol and 10 grams of copper chromite (Harshaw's CU-1106-P) were heated in the stillpot of an efficient fractionating column. The distillate was taken off at 10 mm. pressure at such a rate that the head temperature stayed between 127 and 130° C. The reaction is completed in 12-16 hours. One hundred eighty-five grams of distillate was recovered. Infrared spectroanalysis and the physical properties, B.P.₁₀ mm. 127-130° C., D₄²⁵ 0.918, N_D²⁵ 1.4467, α_D²⁵ (10 cm. tube) +8.63°, of the distillate indicated that it was 90-95% 2-hydroxy-2,6-dimethyl-octane-8-al, hydroxy-citronellal, and 5-10% hydroxy-dihydrocitronellol.

EXAMPLE 7

Two hundred grams of 7,8-epoxy-2,6-dimethyl-octane-2-ol and 152 grams of isopropanol were added slowly to a stirred mixture of 53 grams of sodium in 100 ml. of refluxing toluene. The reaction mixture was stirred one hour after all of the epoxide and isopropanol had been added. The excess sodium was removed by adding 50

cc. of methanol. The reaction mixture was then washed with water, and the oil layer fractionated by distillation. Infrared spectroanalysis of the fraction showed that the sodium in isopropanol reduction of 7,8-epoxy-2,6-dimethyl-octane-2-ol gave a product consisting of 45% 2,6-dimethyl-7-octene-2-ol, 15% unchanged 7,8-epoxy-2,6-dimethyl-octane-2-ol, 30% 2,6-dimethyl-octane-2,7-diol and 10% 2,6-dimethyl-octane-2,8-diol.

EXAMPLE 8

Two hundred grams of 2,6-dimethyl-octane-2,8-diol was slowly added to a refluxing aqueous 25% H₃PO₄ solution. The dehydration product was removed by cohobation as fast as possible. One hundred seventy-eight grams of oil was recovered. Infrared spectroanalysis of the oil indicated that it was 50-55% 2,6-dimethyl-1-octene-8-ol, α-citronellol, and 40-45% 2,6-dimethyl-2-octene-8-ol, β-citronellol. The α-citronellol content was determined from the intensity of the characteristic terminal methylene absorption at 11.2μ in the infrared spectrum.

EXAMPLE 9

To 250 grams of acetic anhydride at reflux, 140-145° C., was added slowly 100 grams of 2,6-dimethyl-octane-2,8-diol. When all of the diol had been added, the reaction mixture was washed with water and saponified by refluxing for 1 hour with excess methanolic KOH solution. Infrared spectroanalysis of the oil, recovered from the saponification mixture by washing with water, indicates that it was 75-80% 2,6-dimethyl-1-octene-8-ol, α-citronellol, and 20-25% 2,6-dimethyl-2-octene-8-ol, β-citronellol.

High purity α-citronellol can be produced by efficient fractionation of this mixture, since α-citronellol boils about 2° C. below β-citronellol at 10 mm. pressure.

Refluxing the α-citronellol for 2 hours with an aqueous 25% H₃PO₄ solution changed it to β-citronellol.

EXAMPLE 10

A portion of crude 70-80% alpha-citronellol produced as in Example 9 is treated with 5% of its weight of copper chromite and the mixture is heated to boiling at 100 mm. absolute pressure. The flask containing the reagents is surmounted by an efficient fractionating column. The boiling point of the distillate is about 135° C., and this temperature is maintained at about 134-138° C. by control of the reflux ratio, so that the aldehyde is removed as distillate from the system and most of the unchanged alcohol is returned to the stillpot. The aldehyde content of the material collected is about 90-95%, and it consists of about 70-80% α-citronellal and 20-30% β-citronellal. The physical properties, B.P.₁₀ mm. 127-130° C., D₄²⁵ 0.918, mixture yields pure α-citronellal, B.P. about 136-138° C. at 100 mm. pressure. The structure of this compound is confirmed by its infrared spectrum and by the fact that it yields 2,6-dimethyl-1-octene when reduced by the Wolff-Kishner reaction.

EXAMPLE 11

Two hundred grams of crude glycol mixture produced as in Example 1 by reduction of 7,8-epoxy-2,6-dimethyl-

octane-2-ol is dehydrogenated using 20 grams copper chromite and at a pressure of 10 mm. absolute. The distillate is collected keeping the column head temperature below 133° C. by adjusting the reflux ratio so that glycols are returned to the stillpot for further contact with catalyst while lower boiling products, chiefly hydroxycitronellal and 2,6-dimethyl-octane-7-one-2-ol, are removed from the head of the column. After about one hundred grams of distillate is removed, additional crude glycol mixture containing 1% copper chromite suspended in it is added to the stillpot at about the same rate as distillate is removed from the head. Five hundred grams of the glycol mixture containing 5 grams catalyst is added over a period of about 30 hours, at which time only about 75 grams of unreacted glycol mixture remains in the stillpot.

Refractionation of the distillate produces high quality hydroxycitronellal and pure 2,6-dimethyl-octane-7-one-2-ol, B.P. 123° at 10 mm. The structure of this compound is proved by hydrogenating it to the previously-identified 2,6-dimethyl-octane-2,7-diol. Upon dehydration by boiling with 30% H₃PO₄, the mixture of glycols yields a mixture composed mainly of β -citronellal and 2,6-dimethyl-2-octene-7-one but containing some Δ^1 products.

EXAMPLE 12

Three hundred grams of crude glycol mixture produced as in Example 1 is dehydrated by adding it slowly to vigorously boiling 30% phosphoric acid so that the monohydric alcohols are removed by steam distillation as they form. The steam distillate is collected in an automatic water trap set to return the aqueous layer to the boiling acid, cohobation. The oil collected is fractionated by distillation at 10 mm. to obtain fractions of fair purity and consisting of 2,6-dimethyl-1-octen-7-ol, B.P. 93-95° C. at 10 mm.; 2,6-dimethyl-2-octen-7-ol, B.P. 96-98° C. at 10 mm.; α -citronellol, B.P. 104-105° C. at 10 mm.; and β -citronellol, B.P. 106-108° C. at 10 mm. The two lower boiling secondary alcohols on hydrogenation each yield 2,6-dimethyl-octane-7-ol. The 2,6-dimethyl-1-octene-7-ol can be converted to 2,6-dimethyl-2-octene-7-ol by refluxing it with 25% phosphoric acid for one hour. Dehydrogenation of the mixture of octenols at 100 mm. also yields a mixture of the α and β forms a citronellal, 2,6-dimethyl-1-octene-7-one and 2,6-dimethyl-2-octene-7-one.

As indicated in the foregoing description and examples, the dehydrogenation step can be carried out on either the glycol or the octenol. Also, as indicated, the tertiary ester or ether can be subjected to any of the treatments shown for the tertiary alcohol. Thus, one can start with an ester or ether of the epoxy-alcohol and carry out the hydrogenation and dehydrogenation steps with the removal of the elements of HX, wherein X is —OH, —OR or



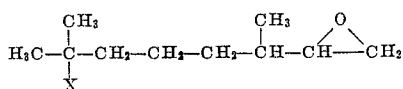
being accomplished at any stage subsequent to the hydrogenation.

Also as indicated, the procedures shown for treatment of the 8-hydroxy compounds are equally applicable to their 7-hydroxy isomers.

This application is a continuation-in-part of my co-pending application Serial No. 576,794, filed April 9, 1956, now U.S. Patent No. 2,902,495.

Having described the invention, what is claimed is:

1. The process which comprises hydrogenating a compound of the general formula



wherein X is a monovalent radical selected from the class consisting of —OH, —OR and



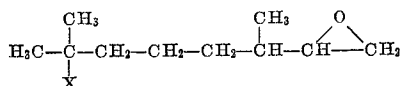
in which R is a lower alkyl radical, to convert the epoxy group to a hydroxy group attached to a carbon atom originally involved in the oxirane ring, and thereafter removing the elements of HX from the number 2 and an adjacent carbon atom and dehydrogenating to convert the hydroxy group attached to the carbon atom originally involved in the oxirane ring to an oxo group, whereby there is produced an oxo-substituted 2,6-dimethyl-octene in which the double bond involves the number 2 carbon atom.

2. The process which comprises hydrogenating 7,8-epoxy-2,6-dimethyl-octane-2-ol to convert the epoxy group into a hydroxyl group attached to one of the carbon atoms originally involved in the oxirane ring, and thereafter subjecting a glycol so formed to a dehydration to remove the elements of water from the number 2 and an adjacent carbon atom and to a dehydrogenation to convert the other hydroxyl group to a carbonyl group whereby there is produced an oxo-substituted dimethyl-octene in which the oxo group is attached to a carbon atom originally involved in the oxirane ring and in which the double bond involves the number 2 carbon atom.

3. The process of claim 2 in which the glycol subjected to the dehydration and dehydrogenation treatments is 1,6-dimethyl-octane-2,8-diol.

4. The process of claim 2 in which the glycol subjected to the dehydration and dehydrogenation treatments is 2,6-dimethyl-octane-2,7-diol.

5. The process which comprises hydrogenating a compound of the general formula



wherein X is a monovalent radical selected from the class consisting of —OH, —OR and



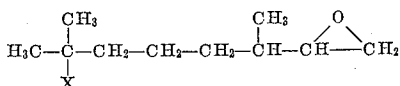
in which R is a lower alkyl radical, to convert the epoxy group to a hydroxy group attached to a carbon atom originally involved in the oxirane ring, and thereafter subjecting the compound thus formed to a dehydrogenation treatment to convert the hydroxy group thus formed to an oxo-group.

6. The process which comprises hydrogenating 7,8-epoxy-2,6-dimethyl-octane-2-ol to convert the epoxy group to a hydroxy group attached to a carbon atom originally involved in the oxirane ring, and subjecting a glycol thus formed to a dehydrogenation treatment to convert the thus-formed hydroxy group to an oxo group.

7. The process of claim 6 in which the glycol is 2,6-dimethyl-octane-2,8-diol.

8. The process of claim 6 in which the glycol is 2,6-dimethyl-octane-2,7-diol.

9. The process which comprises hydrogenating a compound of the general formula



wherein X is a monovalent radical selected from the class consisting of —OH, —OR and



in which R is a lower alkyl radical, to convert the epoxy group to a hydroxy group attached to a carbon atom originally involved in the oxirane ring, and thereafter treating the thus formed compound to remove the ele-

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ments of HX from the number 2 and an adjacent carbon atom to form a 2,6-dimethyl-octenol, and subjecting the thus formed octenol to a dehydrogenation treatment to convert the hydroxy group to an oxo-group.

10. The process which comprises hydrogenating 2-hydroxy-7,8-epoxy-2,6-dimethyl-octane to convert the epoxy group to a hydroxy group attached to a carbon atom originally involved in the oxirane ring, subjecting a glycol thus formed to a dehydrating treatment to remove the tertiary hydroxyl group and form a 2,6-dimethyl-octenol in which the double bond involves the number 2 carbon atom, and subjecting the thus formed dimethyl-octenol to a dehydrogenation treatment to convert the hydroxy group to an oxo-group.

11. The process of claim 10 in which the glycol is 2,6-dimethyl-octane-2,8-diol.

12. The process of claim 10 in which the glycol is 2,6-dimethyl-octane-2,7-diol.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,028,431

April 3, 1962

Robert L. Webb

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 8, line 66, for "physical properties, B.P. 10 mm. 127-130° C., D_4^{25} 0.918," read -- ronellal. Careful refraction-
ation of the crude aldehyde --.

Signed and sealed this 24th day of July 1962.

(SEAL)

Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents