ABSTRACT OF THE DISCLOSURE

Disclosed is a novel compound, 2-(4-methylcyclohex-3-en-1-yl)allyllithium and a process for its production. Also disclosed are processes of converting this novel compound to known and useful limonene derivatives. These derivatives find use mainly as perfume materials.

BACKGROUND OF THE INVENTION

This invention relates to a novel compound, 2-(4-methylcyclohex-3-en-1-yl)allyllithium, and a process for its preparation. As used hereinafter, the novel compound, 2-(4-methylcyclohex-3-en-1-yl)allyllithium will be referred to as metalted limonene. In addition, the invention concerns processes of conversion of the metalted limonene to β-bisabolene, p-mentha-1,8(10)-diene-9-ol, lancedol, lancedol, 9-carboboxy-p-mentha-1,8(10)-diene and 9-carboxymethoxy-p-mentha-1,8(10)-diene.

One of the more important classes of perfume materials has come from the class of materials known as the essential oils. These naturally occurring oils are extracts or distillates of the flowers, fruits, leaves, or roots of many different plants. Each essential oil, though, has an order or flavor that is characteristic of the plant from which it is isolated. The oils usually contain a large number of individual components, the relative proportions and nature of which differ depending on the plant source. However, exhaustive studies in recent years have been conducted to determine the constituents found in the essential oils and, as might be expected, the studies have shown that not all of the constituents of a particular oil contribute to its aroma. Thus any attempt to duplicate the aroma of a naturally occurring essential oil does not necessarily require a synthesis of each individual constituent.

Many essential oils contain substances which have been termed the bisabolene sesquiterpenes. This class of material has been found in many important perfume essential oils such as lavender, lavandin, petitgrain, sandalwood, and various spice oils including ginger oil. These naturally occurring sesquiterpenes are known to possess a wide range of odor properties, many of which are described as being strong, woody, and/or spicy.

In connection with the oil found in the wood of Santalum lanceolatum it was reported by Ruegg, Pfiffner, and Montavon in Recherches (Paris), No. 15, 3 (1966) that one of the constituents, lancedol, possesses a woody odor and is consequently suitable as a perfume material. It was additionally disclosed in the same article that lancedol, the oxidation product of lancedol, possesses an odor reminiscent of sandalwood. However, the syntheses of these materials, as reported by Ruegg et al., supra and by Manjaree, Rios, and Gusman in Tetrahedron, 20, 333 (1964) require many steps and are not commercially feasible. As will be described more fully later, it has now been discovered that these products can commercially be made by a relatively straightforward process through the conversion of a novel intermediate, metalted limonene, to the desired limonene derivatives.

Other essential oils that have found wide use in the flavoring of food products, particularly baked goods, confectionery, and spicy table sauces are oil of ginger and various related spice oils. These materials have also found use in the perfume industry where they impart an individual note to compositions of the oriental type. One of the components responsible for the aroma of these naturally occurring oils is the sesquiterpene β-bisabolene. This material has also been synthesized as reported by Ligouri and Ruzicka in Helv. Chim. Acta, 15, 3 (1932). However, this synthesis suffers from the drawback that it is awkward and commercially impractical. Such disadvantages, though, are eliminated by the novel synthesis described herein. By the present invention the desired product can be formed in a two-step process.

The invention disclosed herein also describes a novel process for the production of p-mentha-1,8(10)-diene-9-ol, a citrus oil constituent. The synthesis of this compound as described hereinafter is simplified by conversion of the metalted limonene to the alcohol.

While the products lancedol, lancedol, and p-mentha-1,8(10)-diene-9-ol are useful in and of themselves as perfume materials, they are also useful in the reconstitution of natural essential oils. By reconstitution is meant the mixing together of all the various individual synthesized components in the same percentages as found in the naturally occurring oil.

Other perfume materials such as 9-carboboxy-p-mentha-1,8(10)-diene and 9-carboxymethoxy-p-mentha-1,8(10)-diene can also be synthesized from the novel intermediate found in the instant invention, i.e., metalted limonene. The materials are known to possess a musty, earthy, minty, floral odor.

SUMMARY OF THE INVENTION

Briefly stated, this invention concerns the discovery of metatalation of a known and readily available compound, limonene, to form a stable intermediate and the further discovery that this intermediate can be converted to a wide variety of known and useful compounds.

Accordingly one of the objects of the present invention is to make an intermediate useful for the synthesis of known and useful perfume and flavor compounds. More specifically, an object of the invention is to produce metalted limonene.

Another object of the invention is to provide a novel process for the conversion of limonene to metalted limonene.

Another object of the invention is to synthesize a variety of materials from metalted limonene.

More specifically, it is an object to convert metalted limonene to lancedol.

Another object is to convert metalted limonene to lancedol.

Another object is to provide a novel process for the production of p-mentha-1,8(10)-diene-9-ol.

Another object of the invention is to provide a process for the production of β-bisabolene from metalted limonene.

A further object is to produce 9-carboxy-p-mentha-1,8(10)-diene.

Still a further object is to provide a process for the production of 9-carboxy-p-mentha-1,8(10)-diene from metalted limonene.

Another object is to provide 9-carboxymethoxy-p-mentha-1,8(10)-diene.

It is also an object to provide a process for the production of 9-carboxymethoxy-p-mentha-1,8(10)-diene from metalted limonene.
Other objects of the present invention will become apparent from a reading of the following discussion and examples.

DISCUSSION AND PREFERRED EXAMPLES

According to the present invention limonene is first metalated to form a stable intermediate suitable for the synthesis of many known and useful compounds. By “metalation” and used herein is meant a reaction involving metal-hydrogen exchange.

The starting material limonene is readily available naturally occurring substance. It is one of the most widely distributed terpenes in nature and is found in several essential oils, in some as the main constituent, especially in citrus oils.

Limonene is found in optically active forms in both the levo- and dextro-rotatory forms as well as the optically inactive or racemic form known as dipentene. The optically inactive limonene or dipentene occurs in various wood turpentine. d-Limonene has been identified in oil of orange (about 90 percent), lemon, mandarin, lime, grapefruit, bergamot, neroli, petitgrain, elemi, caraway, fennel, celery, orthodon oils, etc. 1-Limonene occurs in several pine needle oils, the cone oil of Abies alaba, Russian turpentine oil, star anise, American wormseed, peppermint, spearmint, cajeput, Eucalyptus salteri, Congo copal resin, etc.

Separation of the limonene from essential oils is well known and need not be set out in detail here. Suffice it to say that two methods of obtaining limonene are (1) by fractional distillation; or (2) via certain crystalline adducts, e.g., the tetrabromides, which regenerate the hydrocarbons on debromination with zinc and acetic acid. d-Limonene, l-limonene, and dl-limonene are all commercially available, though, and the isolation or preparation of the starting material forms no part of this invention.

It should be recognized that both optically active forms of limonene, i.e. d- and l-limonene and the optically inactive form, i.e. dl-limonene undergo the same chemical reactions and that the products obtained from each form differ only in optical activity. Thus, products obtained through this invention from the optically active forms are optically active while racemic limonene forms optically inactive products.

The optically active form of limonene used as the starting reactant would be dictated only by the absolute stereochemistry desired for the final product. It has been found that no loss of optical purity occurs during the conversion of either d- or l-limonene to the stable intermediate, metalated limonene, and subsequent reactions to the final product desired. No racemization during the reactions has been detected. This is quite important where production of compounds with a specific configuration is desired. For instance, the naturally occurring β-hibisobene and lanceol are known to occur in nature only in the levo-form. Thus in any strict reconstitution of an essential oil containing either of these two materials it would be necessary to synthesize the levo-form.

However, it should be recognized that the absolute configuration of a material is not always of importance and hence in such cases the stereochemical form of the limonene to be used is of little concern.

Metalation of limonene

According to the present invention limonene is metalated by use of a strong metalating agent, for example, a complex of n-butyllithium and N,N,N′,N"-tetramethylthiylenediamine (TMEDA) which is suggested as a strong metalating agent in recent published articles by Langer in Trans. N.Y. Acad. Sci., Ser. V, 27, 741 (1965) and Eberhardt and Butte, J. Org. Chem. 29, 2928 (1964).

The metalation of limonene is novel as well as the discovery that a stable product is formed therefrom that can be further reacted to form useful compounds. A schematic representation of the reaction is as follows:

While the product formed upon metalation of limonene has been represented by the formula II above, it should be noted that the product formed has not been isolated in pure form and characterized but that II has been theorized to be correct. Another possibility as to the formula of the metalation product would be

Regardless of the correct formula of the reaction product, the resultant product of the metalation of limonene is referred to herein as 2-(4-methylcyclohex-3-en-1-yl)allylithium or simply metalated limonene.

That metalation of limonene at the side chain position occurs is proved by derivatization of the reaction product to form known and/or identifiable products. For instance, the mixture obtained by allowing excess limonene to react with the n-butyllithium-TMEDA complex was treated with carbon dioxide. After esterification with methanol, the product consisted predominantly of the βγ-unsaturated ester represented by III in the following schematic equations:

This set of reactions shows that limonene undergoes metalation at the methyl group attached to the side-chain double bond to form an organolithium species represented by II. This intermediate reacts as an allylic carbonyl on derivatization with resultant substitution of a new group for a hydrogen atom found on the aforementioned methyl group.

The metalation of limonene is quite distinct in that metalation occurs at a position adjacent to only one of the olefinic bonds as noted from the above schematic equations, a result not predictable. This feature is quite important in that it allows the synthesis of very specific compounds without contamination from unrelated by-products. Another important characteristic of the metalated limonene is that it is stable and can be stored at length prior to further reactions with various reagents.

As previously stated, the optical activity or configuration of the limonene depends only on the desired con-
figuration of the product to be formed. If the absolute stereochemistry of the product is unimportant no care need be taken in the selection of the starting limonene.

The metalating agent referred to in the above mentioned articles by Langer and Eberhardt and Butte was found to be quite acceptable for the purpose of the present invention. However, this n-butylolithium-TMEDA complex is but one example of a strong metalating agent useful in the present metalation reaction.

In the present process of metation many organolithium reagents can be employed as the metalating agent. Preferably the organolithium is a primary alkylolithium having from 2 to 10 carbon atoms. For example, ethyllithium n-propyllithium, or n-butyllithium are suitable. Most preferably n-butyllithium is used as the organolithium in the metalating agent.

It has been found that the metalation reaction of limonene does not occur in the presence of an organolithium alone but requires the addition of a complexing agent, preferably a di tertary amine. Accordingly, di tertary amine forms an important part of the metalating agent. Preferably the diamine contains 1 to 4 carbon atoms between the two amino groups. Examples of amines that are useful in the present invention are N,N,N',N'-tetramethylethylenediamine (TMEDA), N,N,N',N'-tetramethyl amine, N,N,N',N'-tetramethylpropylene diamine, sparteine, and 1,4-diazabicyclo [2.2.2] octane (DABCO). TMEDA, DABCO, and sparteine are the preferred ter tary amines. The most preferred tertiary amine is TMEDA.

Theoretically one equivalent of an organolithium is required for each equivalent of limonene. A greater ratio of organolithium to limonene can be used, but since the organolithium is an expensive chemical a large excess is preferably avoided. However, excess limonene can be used with any non-reacted limonene being recovered by distillation prior to final purification of the product. The upper limit of the ratio of limonene to the organolithium is only governed by the limitations imposed by having to separate the recovered limonene from the final product.

In practice it has been found that the range of ratios based on mole equivalents of limonene to organolithium is preferably from one to ten equivalents of limonene for each one equivalent of organolithium. The most preferred ratio for the metation process is two equivalents of limonene for each equivalent of organolithium.

The most preferred ratio of organolithium to amine has been found to be a 1:1 ratio based on mole equivalents. However, mole ratios of 1:0.25-2 of organolithium to amine have been found to be satisfactory. Thus, the preferred ratios based on mole equivalents of organolithium: amine: limonene are 1:0.25-2:1-10.

The metation reaction of the present invention can be carried out by the following procedure. To a container is charged a measured quantity of an organolithium in an inert solvent. While the solution is maintained under an atmosphere of dry inert gas, such as nitrogen or argon, the di tertary amine is added. The solution should be stirred while the addition is made. Limonene is added drop wise to the resulting solution. The resulting mixture is allowed to stand under inert atmosphere for a length of time sufficient to insure a substantial completion of the reaction. Derivatization of the intermediate metalated limonene can now be effected by the direct reaction of the solution with the appropriate reagent, followed by standard work up procedures. Excess limonene, if any, can be recovered by distillation prior to final purification of the product.

The metalated limonene of the present invention can be isolated by evaporating the solution containing metalated limonene to dryness in vacuo. Normally, it is inconvenient to do so since the metalated limonene is employed as an intermediate in the preparation of other compounds by subsequent reactions.

During the metation reaction the reactants are preferably kept free from oxygen and moisture. For this reason a blanket of dry inert gas is maintained above the solution, such as nitrogen or argon as above mentioned. However, it should be realized these gases are but two examples of many gases that can be used. The primary criteria being that the gas preferably be free of moisture and inert.

It is not necessary to carry out the metation in the presence of any solvent other than that in which the organolithium is dissolved. Any solvent that is used for the process should be free of the inert. The preferred solvents are the alkanes and cycloalkanes. Alkanes having having 5 to 10 carbon atoms have been found to be very suitable for the present invention. The most preferred alkane solvent is n-hexane. Cycloalkanes of from 5 to 10 carbon atoms also can be used as a solvent in the metalation reaction with cyclohexane being the most preferred solvent of the cycloalkanes.

The amount of solvent used in the metalation reaction is not critical. The main consideration as to the concentration is the fact that as the dilution increases the reaction rate slows down. It has been found that when undiluted amine and limonene are added to the organolithium solution as described in the sequence above, an amount of solvent can be mixed with the organolithium prior to any limonene or amine additions to make an organolithium solution as dilute as 0.1 molar. A preferred concentration range based on the organolithium is 0.1 to 2 molar. The most preferred amount of solvent is an amount sufficient to make a 1.5 molar solution of organolithium.

While room temperature is satisfactory for the purposes of the metation reaction, slightly higher temperatures can be employed at atmospheric pressure as long as the boiling point of the solvent is not exceeded. The preferred temperature range at atmospheric pressure is 25° C. to 70° C. At higher temperatures some unwanted by-products begin to form. The metation reaction is generally substantially finished after a time ranging from 1 to 24 hours depending on the temperature used. The most preferred time and temperature conditions for the reaction are 12-24 hours and room temperature (20° C. to 30° C.).

β-Bisabolene

The sesquiterpene, β-bisabolene, can be prepared by derivatization of metalated limonene. If it is desired to obtain the naturally occurring β-bisabolene or to reconstitute an essential oil, consideration must be given to the optical configuration of the starting reactant used in producing metalated limonene. Once this determination is made the process can be carried out with the assurance that the final product will have the same absolute configuration as the limonene prior to any reactions. For instance, if it is desired to reconstitute an essential oil, the naturally occurring levo-form of β-bisabolene is preferred. Accordingly, the levo-form of limonene would be utilized in the metation process. Further reaction of this Ilimonene would occur without any racemization with the resultant product free from any contamination by its enantiomers. Of course, frequently the absolute stereochemistry involved will be of no consequence, in which case the d,l, or dl-limonene can be used.

Regardless of the limonene used, however, subsequent chemical reactions will proceed in the same manner.

One of the advantages of forming β-bisabolene according to the present process is that it can be produced by a "one step" process. That is, after limonene is metalated to the stable intermediate, metalated limonene, it does not have to be separated from the reaction mixture but rather, the desired reactant can simply be added with formation of the desired final product. Subsequent separation techniques are used to purify the final product.
In the present invention to form the β-bisabolene, it is necessary to react the metalated limonene with a 1-halo-3-methyl-2-butene according to the following:

\[
\begin{align*}
\text{Li}^+ & \quad \text{CH}_2\text{CH}_3 \quad \text{CH}_2\text{CH}_3 \quad \text{CH}_2\text{CH}_3 \quad \text{CH}_2\text{CH}_3 \\
& \quad + \quad \text{(CH}_2\text{H})_3\text{C} = \text{CHCH}_2\text{X} \quad \rightarrow \\
\text{CH}_2\text{CH}_3 \quad \text{CH}_2\text{CH}_3 \quad \text{CH}_2\text{CH}_3 \quad \text{CH}_2\text{CH}_3 \\
\end{align*}
\]

(β-bisabolene)

where X = Br, Cl, or I.

A process for the production of IV is carried out using metalated limonene as the starting reactant. Metalated limonene is produced in the manner discussed above. To a cooled solution containing the metalated limonene, 1-halo-3-methyl-2-butene is added dropwise. An atmosphere of inert gas is maintained during this addition. The rate of addition is adjusted so as to maintain the solution in a cooled state during the exothermic reaction. After the addition is complete the mixture is allowed to warm to room temperature and water is added dropwise. The organic phase is next diluted with ether and separated. The aqueous solution is extracted with ether. The combined organic solutions are washed successively with aqueous sodium chloride, e.g., 15%, hydrochloric acid, e.g., 3 M, aqueous sodium bicarbonate, e.g., 5%, again with aqueous sodium chloride, and dried and evaporated, Excess limonene, if any, is separated from the resulting liquid by distillation. The colorless oil that remains comprises β-bisabolene and 4,4-dimethyl-2-(4-methylcyclohex-3-en-1-yl)hexa-1,3-diene. These are separated and purified by preparative gas-liquid phase chromatography (GLPC) followed by molecular distillation, or by careful fractional distillation.

The reaction of the halide with metalated limonene is instantaneous and exothermic; thus, the reaction should be carried out at a reduced temperature. Temperatures as high as the boiling point of any inert solvent that is used can be employed but the preferred temperature range is -70°C to 25°C. The most preferred temperature range is -70°C to -20°C.

Oxidation

As a part of the present invention it has been discovered that the metalated limonene can also be used as an intermediate in the synthesis of a compound that is not only useful in itself, but also in the synthesis of other known and useful compounds. The oxygenation of metalated limonene followed by reduction of hydroperoxide intermediates is represented by the following schematic route:

\[
\begin{align*}
\text{L}^+ & \quad \text{CH}_2\text{CH}_3 \quad \text{CH}_2\text{CH}_3 \quad \text{CH}_2\text{CH}_3 \quad \text{CH}_2\text{CH}_3 \\
& \quad + \quad \frac{1}{2} \text{I}_2 \rightarrow \text{H}_2\text{O}, \text{Na}_2\text{S}_2\text{O}_3 \rightarrow \\
& \quad \text{CH}_2\text{CH}_3 \quad \text{CH}_2\text{CH}_3 \quad \text{CH}_2\text{CH}_3 \quad \text{CH}_2\text{CH}_3 \\
\end{align*}
\]

Metalated Limonene

p-Mentha-1,8(10)-dien-9-ol

p-Mentha-1,8(10)-dien-9-ol

V.

Both the acid VI and the ester III are useful as synthetic perfume ingredients possessing a fruity, musky, earthy, floral, minty, fatty, sharp aroma. A portion of a metalated solution prepared in the manner above described is added rapidly to a slurry of Dry Ice in ether, or in the alternative, carbon dioxide gas is passed through a cooled metalated limonene solution. When the resulting mixture warms to room temperature, water is added, the layers separated, and the aqueous layer is extracted with ether. The ether solution can be
dried and evaporated to recover any excess limonene. The aqueous solution is acidified with dilute hydrochloric acid, extracted with ether and then the ether solution is dried and evaporated to give the acidification product, VI. A solution of this material in methanol containing sulfuric acid was then cooled, and gas was blown into water. The resulting mixture is extracted with ether, and the resulting ether solution then washed with dilute aqueous sodium bicarbonate, water and dried and evaporated. Fractional distillation of the residue produces the ester III.

Compounds VI and III are both isolated by fractional distillation after their respective formations in the process as above described.

The formation of metalted limonene is exothermic and occurs instantaneously. The temperature during the formation should remain below 25°C, though it is possible to use higher temperatures. The preferred temperature range when carbon dioxide gas is passed into a metalted limonene solution is 70°C to ±25°C.

The above reactions involving the metalted limonene are preferably conducted in an atmosphere free from air or moisture to avoid unwanted by-products. The following examples are introduced for the purpose of illustrating various processes found in the instant invention.

Example I (metalted limonene).—A flame-dried 500 ml. round-bottom flask, fitted with a magnetic stirring bar, pressure-equalized addition funnel, and gas inlet tube, was charged with 200 ml. (0.30 mole) of 1.5 M n-butyllithium in n-hexane. The contents of the flask were maintained under a static atmosphere of dry, inert gas (nitrogen) at all times. To the stirred solution was added dropwise 45 ml. (35 g., 0.30 mole) of dry TMEDA. A crystalline precipitate formed during the mildly exothermic reaction, which resolved when the addition was complete. To the resulting yellow solution was added dropwise 100 ml. (84 g., 0.62 mole) of either d- or l-limonene. Stirring was continued for 1 hour, and the solution became dark red in color. The solution was allowed to stand overnight at room temperature (25°C) prior to further use.

Metalted limonene is isolated by evaporating the solution to dryness in vacuo.

In the above reaction other organolithiums such as ethyllithium or n-propyllithium as well as other diisocyanates such as tetramethylethylenediamine, tetramethylpropyленediamine, sparteine, or DABCO can be substituted on an equal mole basis for the n-butyllithium and/or TMEDA, respectively, with equivalent results, i.e. metalted limonene is formed.

Example II (β-bisabolone formation).—A solution of metalted limonene was prepared in the manner described above from 67 ml. (0.10 mole) of 1.5 M n-butyllithium in n-hexane, 15 ml. (11.7 g., 0.10 mole) of TMEDA, and 33 ml. (27.7 g., 0.20 mole) of l-limonene. The reaction flask was fitted with a low temperature thermometer and a pressure equalized addition funnel. The solution was stirred and cooled to 60°C while static argon atmosphere in the system was maintained. 15.2 g. (0.10 mole) of 1-bromo-3-methyl-2-butenene was added dropwise via the addition funnel. The rate of addition was adjusted so that the solution temperature did not exceed 40°C. The reaction mixture was allowed to warm to room temperature, and 50 ml. of water was added dropwise. The organic phase was diluted with ether and separated, and the aqueous solution was extracted with three 25-ml. portions of ether. The combined organic solutions were washed successively with 50 ml. of 5% aqueous sodium chloride, 75 ml. of 3 M hydrochloric acid (the acid-water solution was backwashed with ether), 50 ml. of 5% aqueous sodium bicarbonate, 50 ml. of 5% aqueous sodium chloride, and were dried and evaporated. Recovered limonene (13.8 g.) was separated from the resulting liquid by distillation through a 20 cm. Vigreux column, B.P. 66–69°C (17 mm.). Distillation of the residue through a short-path apparatus gave 3.0 g. of additional limonene and 8.64 g. (42% based on n-butyllithium, 33% based on limonene consumed) of a colorless oil, B.P. 60–80°C (0.10 mm.). GLPC analysis showed this material consisted of a 1:4 mixture of 4,4-dimethyl-2-(4-methylcyclohex-3-ene-1-yl)-hexa-1,5,1-diene and 1β-bisabolene. These were separated and purified by preparative GLPC followed by molecular distillation. The infrared spectrum of the 1β-bisabolene so obtained was identical in all respects with published spectra of natural 1β-bisabolene.

Example III.—A procedure similar to Example II was carried out using d-limonene. d-β-Bisabolene was obtained having spectral properties identical with those of the 1-enantiomer.

In Examples II and III above 1-chloro-3-methyl-2-butene or 1-iodo-3-methyl-2-butene can be used in place of the 1-bromo-3-methyl-2-butene with equivalent results.

Example IV.—(oxygenation of metalted limonene).—A solution of metalted limonene was prepared in the manner of Example I from 50 ml. (0.075 mole) of 1.5 M n-butyllithium in n-hexane, 11.25 ml. (8.77 g., 0.075 mole) TMEDA, and 25.0 ml. (24.0 g.) of l-limonene. The reaction flask was fitted with a low temperature thermometer and a gas inlet tube extending beneath the surface of the liquid. The solution was stirred and cooled to 35°C while static argon pressure in the reaction flask was maintained. Air was then passed through a column of Drierite, was bubbled through the solution via the gas inlet tube, and the rate of addition of air was regulated so that the solution temperature did not exceed 20°C. When the exothermic reaction had ceased, the cooling bath was removed and the solution was allowed to warm to room temperature (the air addition was stopped when the temperature reached 0°C). After cautious, dropwise addition of 15 ml. of water, a solution of 18 g. of sodium sulfite in 70 ml. of water was added, and the resulting two-phase mixture was stirred vigorously for 17 hrs. The layers were separated, and the aqueous solution was extracted with three portions of ether. The combined organic solutions were washed successively with 100 ml. of 5% sulfuric acid containing 5% potassium iodide, 140 ml. of 5% sulfuric acid, and 100 ml. of water. The latter two washings were back-extracted with ether, and the combined ether solutions were dried and evaporated. Recovered limonene (12.6 g.) was separated from the resulting liquid by distillation through a 20 cm. Vigreux column, B.P. 67–69.5°C (18 mm.). Distillation of the residue through a short-path apparatus gave 3.74 g. (51%, based on n-butyllithium) of p-metha-1,8(10)-diene-9-ol as a faintly yellow oil, B.P. 66–71°C (0.1 mm.). GLPC purity 97%. The analytical sample was obtained as a colorless oil after purification by preparative GLPC followed by molecular distillation. This alcohol possesses a camphoraceous, minty, soapy, piney odor.

Example V (carbonation of metalted limonene).—A solution of metalted limonene was prepared in the manner of Example I from 40 ml. (0.064 mole) of 1.6 M n-butyllithium in n-hexane, 9.6 ml. (7.5 g., 0.065 mole) TMEDA, and 21.2 ml. (17.8 g., 0.13 mole) of d-limonene. A 60-ml. portion of this solution was added rapidly by syringe to a slurry of Dry Ice in ether. When the resulting mixture had warmed to room temperature, water was added, the layers were separated, and the aqueous layer was extracted with two additional portions of ether. The combined ether solutions were dried and evaporated to give 10.2 g. of recovered limonene. The aqueous solution was acidified with dilute hydrochloric acid, extracted three times with ether, and the combined ether solutions were dried and evaporated to give 6.0 g. of the liquid acid VI, 9-carboxy-p-metha-1,8(10)-diene. A solution of this material in 100 ml. of methanol containing 1 ml. of concentrated sulfuric acid was heated to
reflex for 2.5 hr., cooled, and poured into water. The resulting mixture was extracted with three portions of ether, and the combined ether solutions were washed successively with dilute aqueous sodium bicarbonate, water, and were dried and evaporated. Fractional distillation of the residue (5.3 g.) through a short Vigreux column gave a total of 1.98 g. (19% based on n-butyllithium, 25% based on limonene consumed) of 2-carbomethoxy-p-menth-1a,8(10)-diene as a colorless oil in three fractions: fraction 1, 0.93 g., B.P. 62-67°C. (0.2 mm.); fraction 2, 0.61 g., B.P. 67-75°C. (0.2 mm.); fraction 3, 0.44 g., B.P. 75-91°C. (0.2 mm.). The purities of these fractions determined by GLPC were 92%, 90%, and 72%, respectively. The analytical sample was obtained from fraction 1 by preparative GLPC. This methyl ester was found to possess a fruity, musty, earthy, floral, minty, fatty, sharp aroma.

What is claimed is:

1. 2-(4-methylcyclohex-3-en-1-yl)allyllithium.
2. A process of producing 2-(4-methylcyclohex-3-en-1-yl)allyllithium comprising contacting limonene with a strong metalating agent consisting of a primary alkyl-lithium having from 2 to 10 carbon atoms and a di-tertiary amine having from 1 to 4 carbon atoms between the amino groups.
3. The process of claim 2 wherein the strong metalating agent comprises a n-butyllithium-N,N,N,N'-tetramethylethylenediamine complex.