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Rostov-on-Don State University

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Progress in the Synthesis of Perfumes Based on Pinenes†

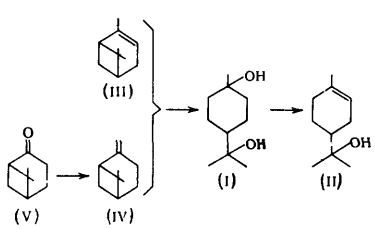
Y.-R.Naves

Turpentine was known in far antiquity. As is well known, it was obtained by steam distillation of various types of pine. Rosin and resins are obtained simultaneously.
All these products were used in the construction of ships. Turpentine was first produced in the XVIth century in North America, where there were vast areas of pine forests in North and South Carolina, Georgia, Alabama, and Virginia and where there was a market for these products, and they became widespread in the XVIIth century. The use of turpentine for the production of varnishes, paints, etc. began about 1830-1840.
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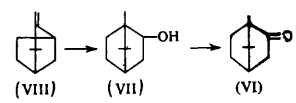
1. Turpentine and the Chemistry of Perfumes

Turpentine was first used as a raw material for the manufacture of perfumes at the end of the XIXth century. In 1827 Vogel obtained terpene (I), which Tilden in 1878 and Wallach in 1885 dehydrated to terpineol(II), and Flavitskii obtained terpineol directly from turpentine in 1879. In France the industrial production of terpineol was the consequence of work carried out by Bouchard and Bouari (1866) and Lafonte (1889).

The structure of α-pinene (III), the principal constituent of turpentine, was suggested by Wagner in 1894 and firmly established by Bayer two years later. The structure of β-pinene (IV) was established by Wallach in 1907 as a result of the synthesis of this terpene from norpinone (V). The first accurate analysis of a mixture of α- and β-pinenes was effected by Darmu in 1911 on the basis of measurements of optical rotatory dispersion.



Camphor (VI) was known in the Far East before recorded time. It was introduced into Europe by the Arabs. Reluz obtained it by the oxidation of borneol (VII) in 1841. At the end of the last century camphor became an important raw material for the manufacture of celluloid and smokeless powders. Bredt established the structure of camphor in 1893, but its synthesis, effected from the pinenes through the intermediate production of camphene (VIII), borneol, and isoborneol, was used industrially only until 1920.



Up to 1940 the pinenes were used for the production of terpineols, borneol, isoborneol, and their esters, and camphor. The position then changed sharply. This progress was due to the efforts of the producers of turpentine to increase its consumption and thanks to the wish of the synthetic perfumes industry to be freed from the use of natural ester oils, the difficulty of supply, variable quality, and high cost of which hindered the further development of this sector of industry.

I will not dwell on the papers dealing with the development of the chemistry of camphene, borneol, isoborneol, and camphor, and also terpenophenols, since most of the terpenophenols were first obtained in the USSR at the All-Union Scientific Research Institute for Synthetic and Natural Perfumes, where in this field also very interesting work is now being carried out.

This review will give the progress reached in effecting the opening of the bicyclic system of the pinenes and their derivatives into compounds of the monocyclic and aliphatic series.

The acid-catalysed decyclisation was effected even longer ago, since the production of terpineols was realised

† Paper read at the All-Union Scientific Research Institute of Synthetic and Natural Perfumes, Moscow, 1967.

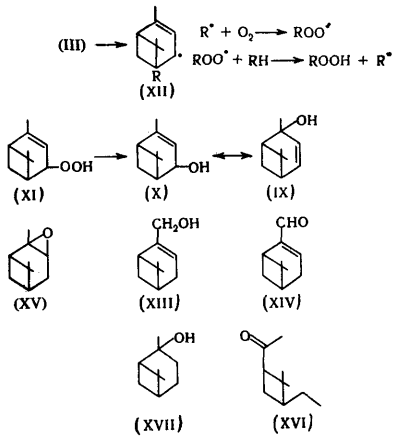
by industry seventy-five years ago. The application of this reaction to bicyclic derivatives of pinenes led to new methods for the production of menthones, menthols, carbeols, and carbone. However, the most progress was achieved in decyclisation by the pyrolysis of pinenes, pinanes, verbenols, and pinanols. These reactions opened the way to the production of aliphatic terpenes and their derivatives, such as linalool, geraniol, nerol, α- and β-citronellols, α- and β-elgenols, α- and β-citrals, citronellals, α- and β-elgenones, hydrohydroxycitronellal, and pseudoionones. The syntheses of these substances also open new paths for the production of menthols.

Many of these syntheses could not be carried out without the development of new methods for the production of verbenols, pinanols, and other similar compounds based on the production of oxides and hydroperoxides.

2. Production of Oxides and Hydroperoxides

The oxidation of α-pinene with or without the use of photosensitizers followed by the reduction of the hydroperoxides formed gives pin-3-en-2-ols (IX) and their allyl isomers—verbenols (X)—pinan-2-ols (XVII), and also verbanols.

According to Dupont[1], the primary products of the oxidation of α-pinene (III) are verbenyl hydroperoxides (XI), which are catalysts for the formation of the free radicals (XII), which initiate chain reactions. The mechanism of these reactions was also studied by Schenk and coworkers[2].



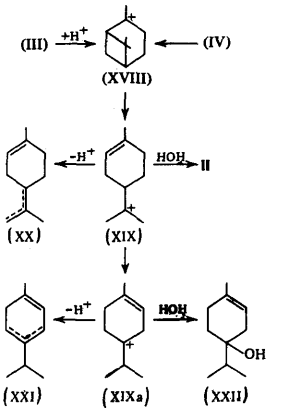
The production of hydroperoxides is accompanied by the formation of pinene oxides by the Prilezhaev reaction. As a result of all the reactions in the oxidation of α-pinene (III) after the reduction of the hydroperoxides a mixture is obtained which contains pin-3-en-2-ol (IX) (predominantly the *cis*-isomer), verbenols (X), verbenone, myrtenol (XIII), myrtenal (XIV), and α-pinene oxide (XV).[3,4] Here (−)α-pinene corresponds to (+)-pinenols, (−)-*trans*-verbenol, (+)-*cis*-verbenol, (−)-verbenone, and (+)-α-pinene oxide. The pinenols can be isomerised into the verbenols (X) by the action of hot water or dilute alcohols. The hydrohalogenation of verbenol leads to verbenyl halides, acetylation with acetic anhydride in the presence of sodium acetate gives *trans*-verbenyl acetate principally. Oxidation with chromium(VI) oxide leads to verbenone[5,6]. The hydrogenation of verbenols over copper chromite at 200°C leads to the formation of a mixture of isoverbanol and neo-isoverbanol[7].

Fischer and coworkers[8] studied the formation of hydroperoxides of pinanes. A product containing 85–90% hydroperoxide is obtained at 40–45% oxidation in 85–86% yield on the pinane used. The decomposition of the hydroperoxides in the presence of sodium methoxide leads to both 1-aceto-3-ethyl-2,2-dimethylcyclobutane (XVI) and pinan-2-ol (XVII) in 50% yield.

3. Decyclisation Catalysed by Acids

Although the opening of the four-membered ring of pinenes by acids has long been known[9,10] its mechanism was established with certainty only in 1947, by Moser[11,12]. In the presence of a proton α-pinene (III) or β-pinene (IV) form a carbonium ion (XVIII). The breaking of the four-membered ring is accompanied by transfer of the positive to the $C_{(8)}$ of the *p*-menthane system and the formation of a double bond in position 1 (XIX). This carbonium ion can be isomerised into (XXa). The removal of a proton leads either to the formation of dipentene and terpinolene (XX) or α- and β-terpineols (XXI). The migration of a double bond to $C_{(2)}$ leads to isoterpinolene and *p*-mentha-2,4-diene.

In the presence of OH ions α-terpineol (II) and terpin-1-en-4-ol (XXII) are formed:



The formation of the terpene (I) proceeds with the intermediate production of a double charged ion (XXIII). Its reaction with water and subsequent dehydration leads to α-, β-, and γ-terpineols, (II), (XXIV), and (XXV).

The formation of terpenes, which is accompanied by the formation of terpene (I) or terpineols, was long considered undesirable. It is now used for obtaining methols through menth-3-ene.

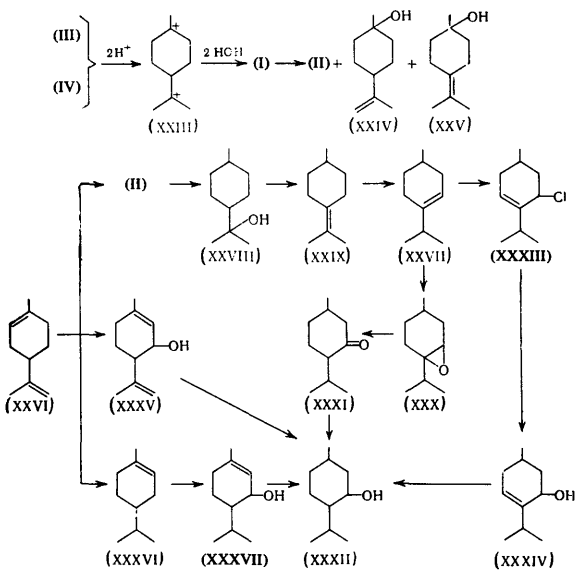
A good yield of monocyclic terpenes with a trace of camphene as impurity is obtained in the treatment of pinenes with ion-exchange resin or aluminosilicate (zeolite)[119]. By carrying out the reaction at a certain temperature, up to 75% limonene or dipentene (XXVI) can be obtained. Limonene (XXVI) exhibits an angle of rotation opposite to that of α-pinene (III), and the same as β-pinene (IV). The optical purity is retained well.

A mixture of monocyclic terpenes with *p*-cymene and camphene as impurities undergoes disproportionation and hydrogenation. Bain and Gary[13] achieved the partial disproportionation in the presence of nickel formate, obtaining menth-3-ene in good yield. Camphene and α-pinene remained unchanged.

Partial hydrogenation over nickel at a low temperature leads to the formation of a mixture[14] of menth-2-ene and menth-4-ene. The latter readily isomerises into menth-3-ene (XXVII) on heating or under the action of acids[15]. As a result, a mixture of menthenes and *p*-cymene is obtained[16-18].

This method of synthesis of menth-3-ene is considerably more economical than the synthesis based on the dehydration of dihydro-α-terpineol (XXVIII) with subsequent isomerisation to (XXIX).[14,19]

The conversion of limonene (dipentene) and menth-3-ene into menthols was effected by different paths. Menth-3-ene (XXVII) is converted into the oxide (XXX) the isomerisation of which leads to menthones (XXXI), and subsequent hydrogenation gives a mixture of menthols (XXXII).[19]



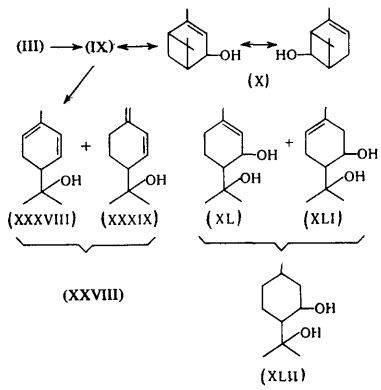
Bain and Webb converted menth-3-ene (XXVII) into 5-chloromenth-3-ene (XXXIII), hydrolysis of which gave *trans*-menth-3-en-5-ol (XXXIV). The last is readily hydrogenated into isomenthol, which can be isomerised into menthol if the temperature and duration of the reaction are sufficient[20].

The oxidation of limonene (dipentene) (XXVI) followed by reduction of the hydroperoxide leads to *p*-mentha-1,4(8)-dien-3-ol (XXXV). The oxidation of carbomenthene (XXXVI)—obtained by selective hydrogenation of dipentene—leads, after reduction, to piperitols (XXXVII), which are then hydrogenated to menthols (XXXII).

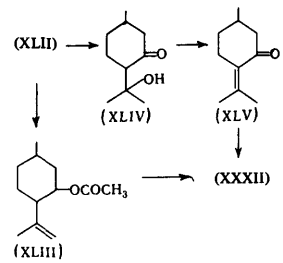
The reduction of hydroperoxides can be brought about by sodium sulphite solution, by the action of triphenylphosphine, or by alkali metal tetrahydroaluminates. The selective hydrogenation of *p*-mentha-1,8-dien-4-ol, obtainable from the hydroperoxides formed in the photosensitised oxidation of limonene (dipentene), leads to terpin-1-en-4-ol (XXII).[21]

The decyclisation of pin-3-en-2-ols (IX) and verbenols (X) takes place just like the decyclisation of α-pinene (III) but in addition a considerable proportion of *o*-mentha-4,6-dien-8-ol is formed. α- and β-8-hydroxyphellandrenes (XXXVIII) and (XXXIX), *p*-menth-1-ene-3,8- and 5,8-diols (XL) and (XLI) and 8-hydroxy-*p*-cymol are obtained predominantly. Decyclisation is brought about by the action of boiling water in the presence of aqueous solutions of zinc chloride, sodium hydrosulphite, and phosphoric acid.

8-Hydroxyphellandrenes (XXXVIII) and (XXXIX) can be converted into dehydro-α-terpineol (XXVIII) and diols into *p*-menthane-3,8-diol, that is, the menthoglycols (XLII).



The latter can be converted into cyclic acetals, which are of interest for perfumery. Reactions with acetic anhydride allow these diols to be converted into acetates of isopulegols (XLIII), from which menthols (XXXII) can be obtained. It is also possible to oxidise these diols to 8-hydroxymenthone (XLIV) which is dehydrated to pulegone (XLV) and hydrated to menthols (XXXII).



Pin-3-en-2-ols (IX) can be converted into pinan-2-ols (XVII), from which α-terpineol (II) was obtained by boiling with water[22].

Pin-3-en-2-ols (IX) and verbenols (X) are converted into verbenyl chlorides and then into verbenyl amines. By hydrolysis of the latter by Bain and Polland's method[23], the corresponding alcohols are obtained, hydrogenation of which leads to menthol.

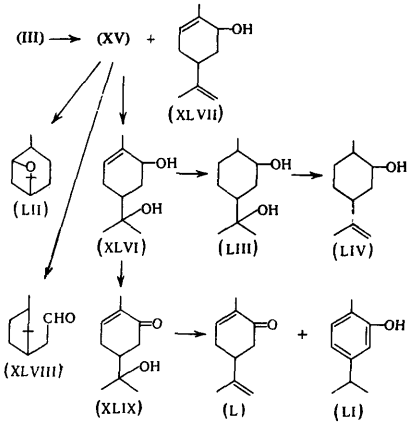
The conversion of α-pinene oxide (XV) into sobrerol or pinol hydrate (XLVI) has long been known. Klein[24], who treated α-pinene oxide (XV) with water or weak alkali solutions in the presence of an antioxidant, obtained predominantly *trans*-sobrerol (XLVI) with the impurity *p*-cymol and other hydrocarbons, and also carveols (XLVII), campholene aldehyde (XLVIII), and *p*-mentha-1,4(8)-dien-6-ol.

This method was perfected by Durbataki and Linder[25], who obtained sobrerol in quantitative yield by acting on α-pinene oxide (XV) with water saturated with carbon dioxide at 30–35°C.

Sobrerols (XLVI) can be oxidised to 8-hydroxycarbone (XLIX), dehydration of which leads to a mixture of carbone (L) and carvacrol (LI).

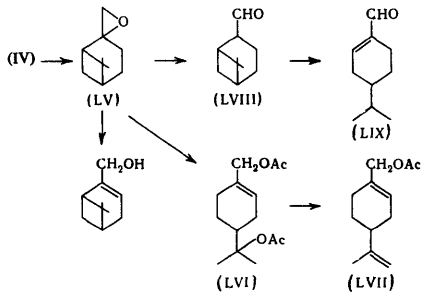
In the usual dehydration of sobrerol the products are pinol (LII) and *p*-cymol, and pyrolysis of pinol diesters gives the esters of carveol (XLVII) in good yield[26]. Thus in the pyrolysis of the diacetates at 162–205°C, 60% of a mixture of acetates of *cis*- and *trans*-carveol is obtained

together with *p*-cymol, *p*-mentha-1,5(8)-diene, pinol, and other products[27].

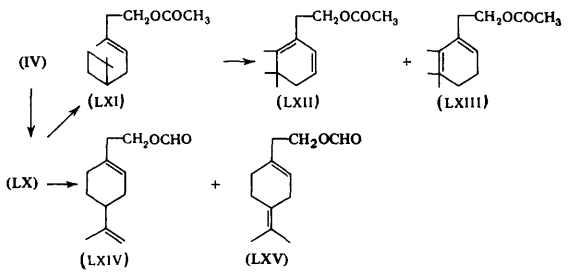


The diacetates of the dihydrosobrerols (LIII) give the acetates of dihydrocarveols (LIV). In this the dihydrocarveols retain the configuration of the dihydrosobrerols, whereas the carveols are racemised.

On treatment with a mixture of acetic acid and acetic anhydride, β-pinene oxide (LV) forms the diacetate of 7,8-dihydroxycarbomenthene (LVI), pyrolysis of which leads to perillyl acetate (LVII), *trans*-myrtanal (LVIII), and phellandral (LIX).[28] Faidutti[29] and Arbuzov[30] obtained myrtanal (LVIII) by treating β-pinene oxide (LV) with zinc chloride, as did Kergomard and Philibert-Bigou[31]. The latter, on using aluminium oxide, obtained a mixture of myrtanal, phellandral, and myrtenol (XIII), free from perillyl alcohol (LXXXV).



Nopol (LX) is an alcohol obtained by the reaction of β-pinene with formaldehyde[14]. Pyrolysis of nopol acetate (LXI) leads to a mixture of α- and β-pyronenecarbinol acetates (LXII) and (LXIII);[32] the treatment of nopol with formic acid gives homoperillyl formate (LXIV) and its isomer (LXV), a mixture of which is used in perfumery.

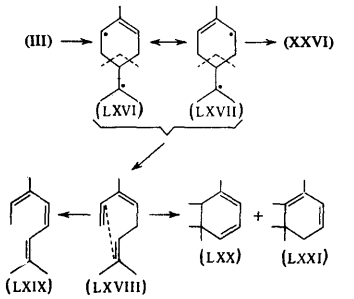


4. Radical Decyclisation

Let us examine reactions associated with the radical decyclisation of pinenes and some of their derivatives: pinanes, pinenols, verbenols, pinanols, verbanols, myrtanols, and epoxypinanes. The main aim of the decyclisation method is the production of aliphatic terpenoids.

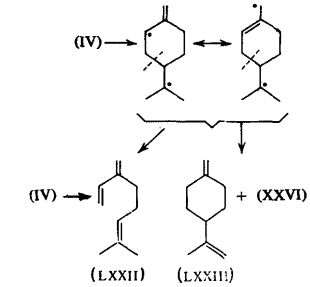
Isomerisation takes place by a radical mechanism[28,33]. Initially, the biradicals (LXVII) and (LXVI) are formed. Their peculiarity is that one of the unpaired electrons participates in the resonance structure of a hybrid of the allyl type, which determines the energy, kinetics, and structure of the products obtainable. The formation of dipentene (XXVI) from the optically active α-pinenes and of limonene from β-pinenes was explained by Burwell[34], starting from the possibility of the migration of hydrogen, which was established by molecular models.

In the decyclisation of α-pinene, in addition to dipentene (XXVI)[35,36], β-ocimenes (LXVIII) are formed, which on the one hand are isomerised into allo-ocimenes (LXIX) and on the other, are cyclised into α- and β-pyronenes (LXX) and (LXXI)[37-46]. However, it was found possible to limit these isomerisations and obtain β-ocimenes (LXVIII) in good yield:

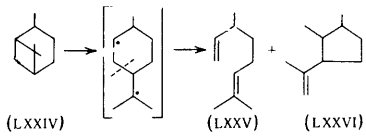


The pyrolysis of α-pinene (III) at 400–450°C leads to the formation predominantly of dipentene (XXVI); at a higher temperature, allo-ocimenes (LXIX)[47] are formed. For the production of β-ocimene (LXVIII) the time of heating had to be shortened to a few milliseconds. Blackmore effected this by using a spiral heated to 500–700°C immersed in the product heated to 50–70°C. The reaction is carried out in a flow system. The α-pinene separated by distillation is returned to the reaction zone. Under these conditions β-ocimene could be obtained in 43–47% yield calculated on the α-pinene (III) used[48,49]. Rectification of the commercial product gave a fraction with 80% ocimenes and 20% dipentene, which was used as such in many syntheses.

β-Myrcene (LXXII), limonene (XXVI), *p*-mentha-1,7(8)-diene (LXXIII), and *p*-cymene are formed in the decyclisation of β-pinene (IV)[50-52]. Myrcene can be isolated from the pyrolysate by rectification, but it is usually considered more economical to use the fraction containing 65–85% myrcene. The impurities are β-pinene, limonene, and—on long storage—camphorenes.



Thermal isomerisation of the pinanes (LXXIV) leads to 2,6-dimethylocta-2,7-diene (LXXV) with retention of the optical activity. The reaction occurs at 550–600°C, predominantly using the *cis*-pinane. The degree of conversion reaches 86%, the yield of dimethyloctadiene 64%. As a result of the cyclisation of dimethyloctadiene, irid-8-enes (LXXVI) are formed[53]:



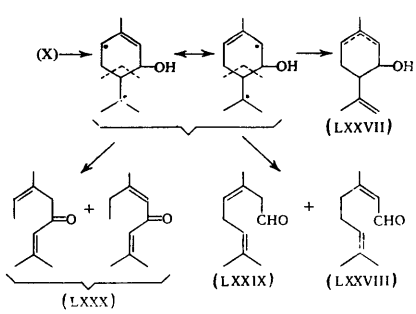
For a certain period myrcene (LXXII) was used for making the β-ocimenes (LXVIII). The isomerisation was effected with good yield in the presence of catalysts—rhodium, iridium, and their chlorides. The reaction proceeds in the presence of 0.5–2% hydrochloric acid at 80–110°C in an inert atmosphere[54]. The same method can be used to convert 2,6-dimethylocta-2,7-diene into 2,6-dimethylocta-2,6-diene and myrcenol into ocimenol.

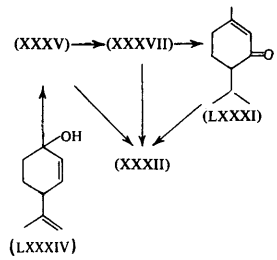
The pyrolysis of verbenols (X)—allyl isomers of pin-3-en-2-ol (IX)—leads to the formation of isopiperitenols and limonenols (LXXVII) and various aliphatic products: citrals (LXXVIII), isocitrals (LXXIX), pseudotagetones (LXXX), and also 2,2,4-trimethylcyclohex-4-enylformaldehyde[55].

The stereochemistry of these reactions is of great importance for the synthesis of (−)-menthol. (−)-α-Pinene (III) gives (−)-*trans*-verbenol with (+)-*cis*-verbenol impurity. Decyclisation of these verbenols leads to menthadienols with the same sign. A mixture of dextrorotatory menthadienols leads to (−)-menthol through the intermediate formation of (+)-neo-menthol, whereas the laevorotatory menthadienols give (+)-menthol through (+)-isomenthol. When special precautions are taken the product will contain a considerable proportion of racemic menthol. To avoid this, the production of (−)-menthol through piperitols was studied[56]. Actually, a mixture of *cis*- and *trans*-piperitols can be isomerised into (+)-*cis*-piperitol by the action of formic acid.

(−)-*trans*-Piperitenol (XXXV), obtainable from (−)-α-pinene, yields (−)-*trans*-piperitol (XXXVII), which is converted into (+)-*cis*-piperitol; the latter is isolated by distillation, then hydrogenated to (+) neo-menthol, which isomerises into (−)-menthol (XXXII). (+)-*trans*-Isopiperitenol leads to (+)-*trans*-piperitol, which is hydrogenated into (+)-isomenthol and isomerised into (−)-menthol.

Instead of this, *cis*- and *trans*-piperitols can be separated by oxidising their mixture to (−)-piperitone (LXXXI), by hydrogenation of which (+)-isomenthone is obtained and from this (−)-menthol (XXXII).





In the pyrolysis of ethers of verbenols, in addition to the esters of isopiperitenols and limonenols a significant proportion of ethers of pseudoverbenols (chrysanthenols) is formed[20]. The ethers can be readily converted into formates or hydrolysed by prolonged boiling with water. The hydrolysis of isopiperitenols leads to the formation of their allyl isomers: *cis*- and *trans*-paramentha-2,8-dien-1-ols. These are separated by fractional distillation and each of them can be converted into a mixture of *cis*- and *trans*-isopiperitenols. All these conversions proceed with retention of the optical activity.

The pyrolysis of verbanols (LXXXII) at 350–700°C leads to 2,6-dimethylocta-2,7-dien-4-ol (LXXXIII)[7,57]. At 450°C 26% of this alcohol is formed together with 19% of an acyclic aldehyde and 20% of an alcohol, which can be oxidised to tagetone and irid-8-en-4-ol (LXXXIV), which is evidently formed in the cyclisation of the alcohol (LXXXIII).

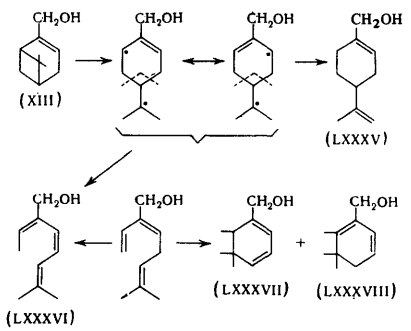
It is interesting to note that in the hydrogenolysis of a mixture of isoverbanol and neoisoverbanol over copper chromite considerable amounts of *o*-menthols are obtained[7].

The pyrolysis of verbanols leads to *cis*-*o*-menth-8-en-3-one, together with other carbonyl compounds[58].

The production of citrals and isocitrals from isopiperitenols and limonenols in an analogous manner to the production of citronellal from isopulegols was effected 40 years ago by Grignard and Doeuvre[59]. The citrals and isocitrals are readily separated by distillation, or a mixture of aldehydes and acetone is condensed in the presence of alkali and pseudoionones are obtained[60].

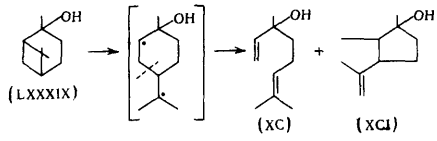
The pyrolysis of myrtenol (XIII) gives ~ 36% perillyl alcohol (LXXXV), 15% 2-methylocta-2,4,6-triene-6-carbinol (LXXXVI) and α- and β-pyronenols (LXXXVII) and (LXXXVIII)[61].

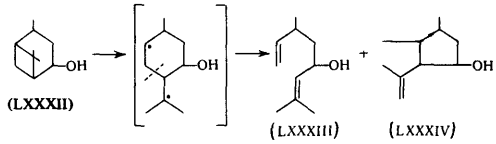
A mixture of *cis*- and *trans*-myrtenols is readily obtained from β-pinene by hydroboronation with subsequent oxidation[62] or by using aluminium alkyls[63]. By the pyrolysis of myrtanols in the vapour phase, Lemberg[64,65] obtained a mixture of 2-methylocta-2,7-dien-6-carbinol and 2-methylocta-2,7-dien-4-carbinol, which are readily separated by fractional distillation



The pyrolysis of pinanols (LXXXIX) is of great interest, since it leads to linalool (XC). Pinanols can be obtained by the hydrogenation of pin-3-en-2-ols (IX) or by starting

from hydroperoxides of pinanes. Pyrolysis is carried out at 600°C in a flow system in the absence of Lewis acids, which bring about dehydration. As a result of the cyclisation of linalool, plinols (XCI) are formed and also 2,6-dimethylocta-2,7-dien-4-ol, 3-ethyl-2,3-dimethyl-cyclobutyl methyl ketone, and α-terpineol (II). *cis*-Pinanol gives 95% linalool *trans*-pinanol 75%. (+)-*cis*- and (−)-*trans*-pinanol corresponds to (−)-linalool, (−)-*cis*- and (+)-*trans*-pinanol to (+)-linalool[66,67]. The cyclisation of linalool at 650°C leads to the formation of four stereoisomeric plinols[68].





cis-Dihydronopol, readily obtained by the catalytic hydrogenation of nopol (LX), forms, after pyrolysis at 500–600°C, a mixture containing 50% 2-methyl-6-vinyloctan-8-ol. Partial hydrogenation of this alcohol at the vinyl group gives homocitronellol (6-ethyl-2-methyloctan-8-ol).[69]

5. Conversions of Aliphatic Hydrocarbons

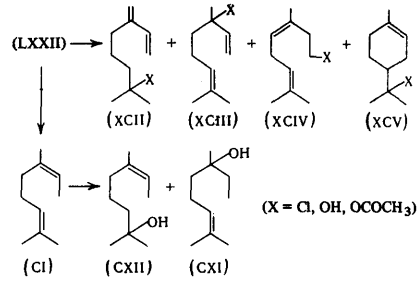
The production of almost unlimited amounts of β-myrcene (LXXII), β-ocimene (LXVIII), allo-ocimenes, and products of their partial hydrogenation, namely, 2,6-dimethylocta-2,7-diene made possible a large number of syntheses of commercial interest.

The main reactions of these hydrocarbons are as follows: (1) the addition of organic acids for the production of esters (the Bertram–Wallbaum reaction): (2) the oxidation of double bonds with subsequent isomerisation to aldehydes or ketones or hydrogenation to alcohols; (3) the production of organometallic derivatives with subsequent conversion into alcohols; (4) the addition of halogens, hydrogen halides or hypohalogen acids with subsequent pyrolysis of the hydrohalides, dehydration of the halogenohydrins to unsaturated halogen derivatives or dehydrohalogenation to epoxides; the hydrolysis of halides to alcohols or conversion into esters by reaction with salts or organic acids.

In incomplete addition, the double bonds compete with one another. In instances when it is possible allyl rearrangements take place.

Syntheses from β-myrcene (LXXII) have most value. In this way above all linalool (XC), geraniol, nerol, and their esters are obtained.

β-Myrcene is converted into the monochlorides (XCII)–(XCV). Without a catalyst the predominant products are the chlorides of myrcenol, terpineol, and borneol. The amount of these chlorides, especially myrcenyl chlorides, can be decreased by carrying out the hydrochlorination at low temperature in



the presence of an antioxidant and a catalyst—copper or a copper(I) salt[70]. The addition of hydrochloric or hydrobromic acid is controlled spectrometrically by the disappearance of the conjugated double bond. Increase in temperature and increase in the amount of catalyst decreases the proportion of linalyl chloride and increases the content of geranyl and neryl chlorides. Under optimal conditions the final concentration of myrcenyl chloride < 10%; without a catalyst, its concentration reaches 50–60%.[71] Conversion of the halides into esters in the absence of a catalyst does not give good results. The catalysts used can be bases containing nitrogen or phosphorus[72–74], for example, trimethylamine, triethanolamine, phosphonium salts or derivatives of phosphorus(III) (phosphines) capable of forming quaternary derivatives in the presence of alkyl halides, or even phosphorus[74]. The reaction proceeds in an acid medium, for example, in the presence of acetic acid, which facilitates the formation of esters of linalool[75] or in the presence of bases, which increases the yields of esters of geraniol and nerol. The use of solvents to facilitate the rearrangement is recommended, and dilute dimethyl sulphoxide is also used[73]. The yield of acetates can reach 75–95%.

To diminish the formation of myrcenyl chloride dihydrochlorination of myrcene is carried out[76,77]. This reaction was effected at 10–50°C in the presence of copper chloride. The conversion into the ester was performed in the presence of a base, for example, 1% trimethylamine. The formation of geranyl acetate and neryl acetate is facilitated by raising the temperature and increasing the duration of reaction. ~ 50% of the α-isomers are formed.

Good results were obtained in the hydrolysis of products of the addition of two molecules of hydrochloric acid[78,79]. The reaction was brought about by using an aqueous suspension of calcium carbonate in the presence of an emulsifier. In this way 2-hydroxy-2,3-dihydro-linalool, -geraniol, and -nerol were obtained. 2,3-dihydro-2-hydroxylinalool can be converted into isomers by the action of formic acid, with a yield of 73–75%. The dehydration of glycols leads to a mixture of isomers of α- and β-linalool, geraniol, and nerol. Carrying out the dehydration without appropriate precautions leads to the production of ocimenol and α-ocimenes. The production of β-ocimene from α-pinene in good yield allows β-myrcene to be replaced by this terpene.

The mixture of chlorides obtained in monohydrochlorination, which contains geraniol and neryl chlorides can be converted into citrals by the Kröhnke procedure with the

Liebermann method[80]. Pseudoionones are obtained by reaction in a medium of acetone.

The production of geraniol and nerol from pinenes made possible the synthesis of citral. It is difficult to carry out the catalytic dehydrogenation in a directed manner. In the presence of copper catalysts disproportionation occurs, leading to the production of citronellal[81,82]. The oxidation of geraniol and nerol with chromic acid leads to citral in 80–85% yield. It gives better results than oxidation with manganese dioxide (68%) or by functional exchange[83,84]. The Openhauer reaction with aluminium alkoxides in an acetone medium leads to pseudoionones[85–89].

Whereas the oxidation of 2,3-dihydro-2-hydroxylinalool gives only 44–47% 2,3-dihydro-2-hydroxycitral, which is more readily hydrogenated to 2,3-dihydro-2-hydroxycitronellal than dehydrogenated to citral, 2,3-dihydro-2-hydroxygeraniol and -nerol can be converted over copper chromite directly into hydrohydroxycitronellal in 90–95% yield[90,91].

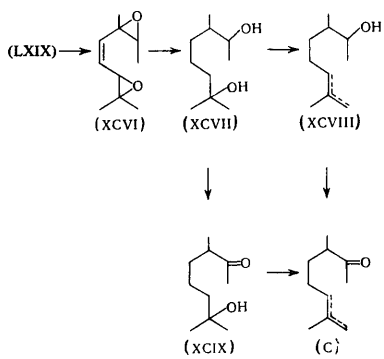
Ocimenol can be obtained from β-myrcene through the intermediate formation of a sulphone obtainable by the action of sulphur dioxide at 50–100°C. The sulphone is hydrated by 40–60% sulphuric acid and the hydrate decomposed by heating to 120–170°C.[92] The decomposition can also be brought about in the presence of 1–2% amine, for example, triethanolamine, or calcium carbonate.

By the action of hydrochloric acid at 20–110°C myrcenol and ocimenol are converted into a mixture of 2,6,6-trimethyl-2-vinyltetrahydropyran and 2,2-dimethyl-5-(1-methylpropenyl)tetrahydrofuran, used in perfumery.

2-Methylmethylene-6-oct-2-en-8-ol was obtained in 68% yield from β-myrcene by the action of di-isopentylborane (obtained by the reaction of boron hydrides with 2-methylbut-2-ene). This alcohol is readily hydrogenated to citronellol[93].

The monoepoxidation of β-myrcene to β-ocimenes takes place at the double bond in the 2,3-position. Isomerisation of monoepoxides under the action of acids[94] leads to 2,6-dimethylocta-4,6-dien-3-ols.

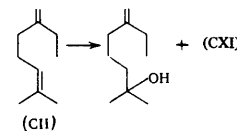
Allo-ocimenes can be used for very interesting syntheses. The polymeric peroxide which is formed on adding oxygen yields the diepoxide (XCVI) on heating; the structure of this was the subject of discussion[95–100]. This diepoxide is readily hydrogenated into *erythro*- and *threo*-2,6-dimethyloctane-2,7-diol (XCVII), partial dehydration of which gives a mixture of the *erythro*- and *threo*-isomers of the α- and β-elgenols (XCVIII), already known under the name of secondary citronellols. The pyrolysis of the diacetates of these glycols leads to acetates of α-elgenol. Oxidation of the glycols with chromic acid leads to hydroxyelgenol (XCIX), which is dehydrated into a mixture of α- and β-elgenols (C).



Theimer[101] hydrochlorinated allo-ocimenes in a flow system. Treatment of the chlorides with water in the presence of an emulsifier leads to a mixture of the alcohols 2,6-dimethylocta-3,5-dien-2-ols and 2,6-dimethylocta-2,4-dien-6-ols. Hydrogenation of this mixture gives the more stable saturated alcohols.

The syntheses starting from 2,6-dimethylocta-2,7-diene (LXXV), obtainable in the pyrolysis of pinane (LXXIV) or by partial hydrogenation of myrcene (LXXII), are of great interest.

The product of the pyrolysis of pinanes is optically active. It includes irid-8-enes (LXXVI)[102,103]. The partial hydrogenation of myrcene (LXXII) is insufficiently selective[104] and the product obtained contains 2,6-dimethylocta-2,6-diene (CI) and 2-methyl-6-methyleneoct-2-ene (CII).



2,6-Dimethylocta-2,7-diene (LXXV) can be converted into β-citronellol (CIII) through organoaluminium compounds by the action of lithium tetrahydroaluminate, or better tri-isobutylaluminium. The organometallic compound is oxidised by moist air and the aluminate formed is hydrolysed to citronellol[99,105–108]. The yield reaches 77%.

In another variant of this synthesis diborane converts 2,6-dimethylocta-2,7-diene (LXXV) into tricitronellylboron[109]; the latter is oxidised to citronellyl borate, from which β-citronellol (CIII) is also obtained by hydrolysis or oxidative hydrolysis with hydrogen peroxide[91,109]. This method, like the method via tricitronellylaluminium, was perfected by carrying out the oxidation in the presence of organo-zinc or -cadmium compounds. The yield is 80%.[110]

(−)-Citronellol is obtained from (+)-α-pinene (III) through the intermediate formation of (+)-dimethyloctadiene, and (+)-citronellol from (−)-α- and (−)-β-pinenes through (−)-dimethyloctadiene[111].

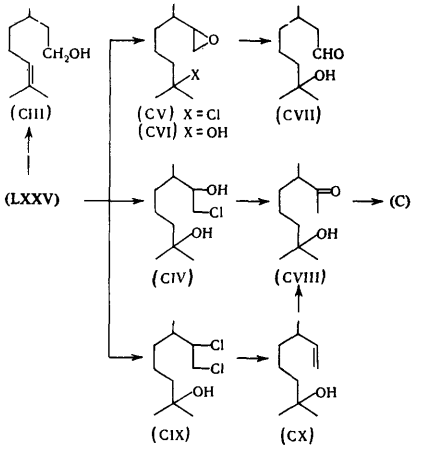
The optically active citronellols prepared in this way can rival the (+)-citronellol obtained by the hydrogenation over Raney cobalt of geraniol and nerol synthesised from α-myrcene and ocimene[112].

There are other methods of obtaining hydrohydroxycitronellol and the corresponding aldehyde, and also elgenol from 2,6-dimethylocta-2,7-diene.

The following schemes are given in Webb's patents[113,114].

A hydrocarbon (LXXV) is converted into 2-chloro-2,6-dimethyloct-7-ene, from which by the action of peracetic acid or through the chlorohydrin (CIV) the epoxychloride (CV) is obtained, hydrolysis of which by an aqueous suspension of $Ca(OH)_2$ gives 7,8-epoxy-2,6-dimethyloctan-2-ol (CVI) in good yield.

Pyrolysis of this product at 250°C leads to hydrohydroxycitronellal (CVII), which can also be obtained through the chlorohydrin. After treatment with lime at 200–210°C a mixture of products is formed, from which via the hydrogen sulphite compound a hydroxycitronellal containing 5–8% α-citronellal is isolated. On boiling the non-aldehyde fraction with sodium in isopropanol it is converted into 2,6-dimethyloct-7-en-2-ol, which can be used for the production of the epoxide (CVI).



In the conversion of the chlorohydrin (CIV) into the epoxide (CVI) a certain proportion of 2,3-dihydro-2-hydroxyelgenone (CVIII) is formed, from which α- and β-elgenones (C) can be obtained.

7,8-Dichloro-2,6-dimethyloctan-2-ol is isolated as an intermediate in the production of the chlorohydrin (CIX). After treatment with potassium hydroxide at 200°C in ethylene glycol, the allene 2,6-dimethylocta-6,7-dien-2-ol is obtained; by catalytic hydrogenation or by reduction with sodium in t-butanol it is converted into 2,6-dimethyloct-7-en-2-ol (CX), which is used again. Under the action of mercury sulphate in sulphuric acid the allene derivative forms hydrohydroxyelgenone (CVIII).

Webb also described[115] the hydrogenation of 7,8-epoxy-2,6-dimethyloctan-2-ol (CVI) to hydrohydroxycitronellol, which on passage over copper chromite forms hydrohydroxycitronellal (CVII) and α-citronellal. It can also be dehydrogenated into a mixture of α- and β-citronellals.

Under the action of hydrobromic acid after Karasch, 2,6-dimethylocta-2,7-diene and 2-chloro-2,6-dimethyloct-7-ene add on hydrogen bromide contrary to the Markovnikov rule. 2,8-Dibromo-2,6-dimethyloctane and 2-chloro-8-bromo-2,6-dimethyloctane are formed, by hydrolysis of which hydrohydroxycitronellol is obtained, which can be dehydrated to a mixture of α- and β-citronellols.

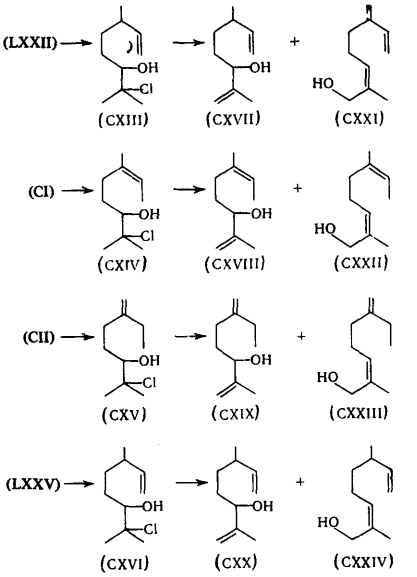
Pyrolysis of the dihalogenides leads to mixtures of the bromides of α- and β-citronellols, with the former predominating.

The production of optically active citronellals from (−)-2,6-dimethylocta-2,7-diene allows (−)-menthol to be synthesised.

We will pay some attention to the production of α-citronellol and α-citronellal free from ester oils and having a more pleasant odour than their β-isomers. It has long been known that α-citronellal is obtained by the dehydration of hydrohydroxycitronellal. It is found among the side-products in the production of hydrohydroxycitronellal by hydration of the hydrogen sulphite compound of β-citronellal. It is also known that its cyclisation into isopulegol is slower than the isomerisation of the β-isomer[7,60,116]. In the production of citral from hydrohydroxygeraniol and nerol, α-citral is formed, the odour of which, however, was not better than that of β-citral.

Partial hydrogenation of β-myrcene (LXXII) leads to not only 2,6-dimethylocta-2,7-diene (LXXV), as already stated, but also to 2,6-dimethylocta-2,6-diene (CI) and to 2-methyl-6-methyleneoct-2-ene (CII). Hydrogenation of β-ocimene (LXVIII) leads mainly to 2,6-dimethylocta-2,6-diene (CI), and hydrogenation of allo-ocimene to 2,6-dimethylocta-2,4-diene.

By the action of hydrochloric acid on 2,6-dimethylocta-2,6-diene (CI) Kitchens[117] obtained dihydrolinalyl chloride, which he hydrolysed to dihydrolinalool (CXI). In this the formation of dihydromyrcenol (CXII) was not noted. On the other hand, Webb succeeded in adding halogen to the second carbon atom of various dihydroterpenes mentioned earlier. The chlorohydrins (CXIII), (CXIV), (CXV), and (CXVI) were obtained by the addition of hypochlorous acid to myrcene (LXXII)[76]. When these products were hydrolysed and the resulting tertiary alcohol was dehydrated, the secondary alcohols (CXVII), (CXVIII), (CXIX), and (CXX), and their allyl isomers (CXXI), (CXXII), (CXXIII), and (CXXIV) were obtained.



The addition of organic acids by the Bertram–Walbaum reaction[118] takes place at the 2,3-double bond. The reaction occurs at 15° and 45°C in the presence of 1–4 parts organic acid containing 0.25–1% sulphuric acid. By replacing the latter by an acid ion-exchange resin, the reaction could be carried out continuously.

The addition of formaldehyde to β-myrcene leads, according to Sommerwell, to a mixture of 3-(4-methylpent-3-enyl)-5,6-dihydropyran and 4-(4-methylpent-3-enyl)-5,6-dihydropyran which can be converted into alcohols and their esters. On carrying out condensation in an organic acid an ester of 2-methyl-6-methyleneocta-1,7-diene-carbinol is also formed.

Webb studied the addition of formaldehyde to dihydroterpenes obtained by partial hydrogenation of β-myrcene and β-ocimene[49]. Heating is necessary, at least to 240°C, better 250–285°C. In the presence of an organic acid a lower temperature is used, for example, 130–160°C in acetic acid. Primary alcohols or their esters are obtained in this way. The alcohols can be converted into aldehydes. According to Webb's results the addition of carbinol takes place at the third carbon atom.

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Hence the development of the chemistry of the pinenes, connected with the use of decyclisation has created a serious basis for the production of many important synthetic perfumes.

The following have been obtained:

1. Aliphatic terpene alcohols and their esters: linalool, geraniol, nerol, α- and β-citronellols, α- and β-elgenols.

2. Aldehydes and ketones and their derivatives: citral, pseudoionones, α- and β-citronellal, hydrohydroxycitronellal, α- and β-elgenones.

3. Monocyclic terpene alcohols: carveols, dihydrocarveol, isopiperitenols, piperitenols, isopulegols, menthols, and the corresponding ketones and aldehydes.

The industrial production of linalool, citral and pseudoionones on a large scale based on pinenes, together with the synthesis of these substances from acetylene made it possible to get rid of the inconvenience due to the instability, the difficulty of acquiring, and the variations in price of the essential oils which were for long the sole source of production of these materials. Synthetic perfumes are obtained at a lower price and with a greater purity than previously from the essential oils. This assists the development of the perfumery industry, especially for the production of mass perfumery. The synthetic products are used to reconstruct many essential oils. Some success was achieved, thanks to carrying out planned and unremitting investigations. It should be noted, however, that the results of these studies are still in the state of being used by only a few powerful industrial groups which produce these products in amounts ranging from a few hundreds to 1000–2000 tonnes per year.

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Givaudan A.G., Geneva, Switzerland