

Chemistry of α -Phellandrene

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(+)- and (-)- α -Phellandrenes [1(a) and 1(b)] are widely distributed in nature. The (+)-isomer occurs in the oil of gingergrass, Manila elemi, bitter fennel, star anise, cinnamon, Spanish dill herb, and *Boswellia serrata*, among others. The (-)-hydrocarbon is found in the oil of *E. dives*, *E. phellandra*, *E. cneorifolia*, pimento, bay, and pepper. (\pm)-Phellandrene has also been described.^{1,2}

α -Phellandrene is used in scents, as a component of artificial essential oils,³ and as an attractive raw material for chemical syntheses. It is therefore of interest to review the significant phases of the chemistry of this p-menthadiene.

Isolation

No technique other than fractional distillation is known to separate α -phellandrene from essential oils. Since the hydrocarbon partially decomposes on distillation at ordinary pressure, the fractionation should be conducted in vacuum.⁴ Even cautious distillation under diminished pressure does not lead to anything approaching quantitative isolation of the terpene owing to its tendency to polymerize.⁵

Perhaps the most trustworthy directions for the isolation of (-)- α -phellandrene are given by Hancox and Jones.⁶ The starting material is *E. dives* oil, which contains pinene, piperitone, and cineole as well as phellandrene. By repeated fractionation, pinene and piperitone are removed, though other workers⁷⁻¹⁰ recommended the use of hot sodium sulfite to extract the ketone. Cineole is eliminated by processing with resorcinol solution. Fractionation at $<45^\circ$ (1.5 mm) yields α -phellandrene, b.p. 39° (4.5 mm), d_4^{20} 0.8369, n_D^{20} 1.4728 and $(\alpha)_D -168.5^\circ$.

(+)- α -Phellandrene, isolated by fractionating the terpene fraction of elemi oil through a column packed with Lessing rings, has b.p. 53°C (11 mm), n_D^{20} 1.4729, d_{20}^{20} 0.8475, $(\alpha)_D^{20}$ 85.5° .¹¹ Earlier literature^{1,2} reported b.p. $175-176^\circ$ (754 mm), d_{15} 0.8440; b.p. 61° (11 mm), d_{15}^{15} 0.8565; b.p. $44-45^\circ$ (4 mm), d_{15}^{15} 0.8470,² $(\alpha)_D^{15}$ 115° ; and n_D^{19} 1.4732 for the terpene. The constants described for (\pm)- α -phellandrene are: (1) b.p. $175-176^\circ$, n_D^{22} 1.4760, d_{22}^{22} 0.8410, and (2) b.p. $63-65^\circ$ (15.5 mm), n_D^{20} 1.4772.¹³

Derivatives

Nitrosite. α -Phellandrene affords a crystalline nitrosite,^{14,15} an exceedingly convenient and rapidly forming derivative. The best procedure for the preparation of the derivative is that of Wallach and Gildemeister.¹⁶

Credit must be given to Schreiner¹⁷ for focusing attention on the two-component nature of the nitrosite derived from (-)- α -phellandrene. Rapid dissolution of the crude nitrosite in boiling ethyl acetate and then chilling in ice-cold water affords long, well-defined needles of (-)- α -phellandrene- α -nitrosite, m.p. $120-121^\circ$, $(\alpha)_D$ 123.5° . On the other hand, addition of 60% ethanol to the ethyl acetate mother-liquor yields a second variety, (-)- α -phellandrene- β -nitrosite, crystallizing in "confused aggregates" m.p. $100-101^\circ$, $(\alpha)_D -36^\circ$; recrystallization of this sample from methanol elevates the m.p. to $105-106^\circ$.

Wallach,¹⁸ following Schreiner, has also isolated the isomeric nitrosites, but these possess the following constants: (-)- α -phellandrene- α -nitrosite; m.p. $113-114^\circ$, $(\alpha)_D$ 142.6° , 135.93° ; (-)- α -phellandrene- β -nitrosite: m.p. 105° , $(\alpha)_D -40.817^\circ$, -40.287° . Perhaps the purest sample of α -nitrosite of (-)- α -phellandrene however, is that prepared by Smith, Hurst and Read, m.p. $121-122^\circ$ (acetone), $(\alpha)_D^{20}$ 142.6° .⁵

The mutarotation of the α -nitrosite under a variety of conditions has also been studied.⁵ For the isolation of the β -nitrosite from crude crystalline nitrosite, Smith, Carter and Read exploit the relative insolubility of the α -isomer in hot carbon disulfide.¹⁹ The β -variety secured by these investigators has m.p. $105-106^\circ$, $(\alpha)_D^{20}$ -160.5° (CHCl_3) and displays mutarotation. Both α - and β -nitrosites are dimolecular.¹⁹

Further scrutiny of the nitrosites of (-)- α -phellandrene by Berry, Macbeth and Swanson⁸ reveals that the α -nitrosite prepared by previous investigators is pure while the β -isomer is not homogeneous. They have standardized the steps for the isolation of homogeneous β -nitrosite, m.p. 96° , $(\alpha)_D^{20}$ -260.1° .

Berry, Macbeth and Swanson⁸ have also produced convincing proof that the labile β -nitrosite is convertible into the stable crystal-

line α -nitrosite. Crystallization of the β -nitrosite from acetone, methanol or other solvents effects fractional conversion into the α -form. This formation explains the discrepancies in the literature concerning the crystal form of the α - and β -nitrosites.^{5,17}

The α - and β -nitrosites of the (+)- α -phellandrene have also been described.¹¹ Constants quoted are: (+)- α -phellandrene- α -nitrosite, m.p. 119°, (α)_D²⁰ -133.8°; (+)- α -phellandrene- β -nitrosite, m.p. 100°, (α)_D²⁰ -198.3°. Transformation of β - into α -nitrosite as well as the mutarotation effects of these derivatives have also been reported.¹¹

Very recently the stereo-structure of α -nitrosite has been elucidated through PMR spectroscopy as (2R,4S,4S), 5-nitroso-2-nitro-1-methyl-4-isopropyl-6-cyclohexene (2).²⁰ The cyclohexene ring exists in half chair conformation with equatorial isopropyl group, pseudo-equatorial nitroso group and pseudo-axial nitro group. The nitrosites are decomposed under alkaline conditions, but no α -phellandrenes are recovered.

Maleic anhydride adduct. An outstanding derivative of the hydrocarbon is the maleic anhydride adduct. Originally discovered by Diels and Alder,²¹ mixing of the benzene solution of the terpene and maleic anhydride, even in the cold, yields the crystalline adduct, m.p. 126-127°. Addition also occurs with ease, in ether,^{22,23} alcohol,²³ or acetone.²³ Of these, acetone is particularly useful because of its volatility, capacity to dissolve reactants and solubility in water.²³ The absolute configuration of the adduct from (-)- α -phellandrene is (1R,2R,3S,4S,5R)-7-isopropyl-5-methylbicyclo-(2.2.2)oct-5-ene-2,3-dicarboxylic anhydride (3).²⁹

Littmann^{24,25} has investigated the mechanism of this diene synthesis. Depending upon experimental conditions, the addition is accompanied by formation of 10% polymer in which the average ratio of maleic anhydride to terpene is of the order 4:3 or 5:4. The empirical formula of the polymer may be C₄₆H₅₆O₁₂ or C₆₀O₁₅.²⁴

This synthesis has also been utilised for detecting^{22,23} and estimating α -phellandrene,^{21,23,26,27} diagnosing relative amounts of the (+)- or (-)- α -phellandrene, and establishing the presence of (\pm)- α -phellandrene.²⁸ In addition, the synthesis is useful in extracting α -phellandrene from essential oils. This will facilitate the examination of other constituents.^{28,30,46}

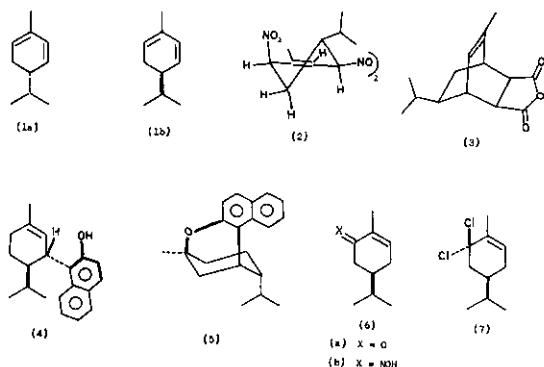
Addition product with β -naphthol. Salfeld^{31,32} has given directions for the preparation of α -phellandrene- β -naphthol adduct, m.p. 130° and of its cyclic isomer, m.p. 105-106°, now shown to be accommodated by structures 4 and 5 respectively.³³

These examples show the applicability of α -phellandrene to the Diels-Alder reaction; with other reaction-partners this might also lead to novel and useful chemicals.

Syntheses

In the synthesis reported by Harris and Johnston,³⁴ the action of phosphorus pentachloride on (-)-carvotanacetone (6a) forms the dihydrochloride (7) which by depletion of hydrogen chloride affords the monochloride (8). Reduction of the latter with zinc dust in alcoholic solution gives (+)- α -phellandrene (1a).

Another preparation by the same investigators³⁴ involves the distillation, under reduced pressure, of the phosphate of 6-amino- Δ^1 -p-menthane (9) available by reduction of carvotanacetone oxime (6b).



Read, Dewar and Galloway³⁵ have described the synthesis of (-)- α -phellandrene starting from (-)-4-isopropyl- Δ^2 -cyclohexene-1-one (10), cryptone. Reaction of this with methylmagnesium iodide yields the tertiary alcohol, (-)-cis- Δ^3 -menthen-1-ol (11a) (?). When boiled with a solution of oxalic acid, the latter is dehydrated to the desired diene.

An ingenious synthesis of (\pm)- α -phellandrene is based on the decomposition of (\pm)-piperityltrimethylammonium iodide (12) by heating with silver oxide and water.³⁶ A similar processing of the (-)-quaternary compound yields (+)- α -phellandrene. On the other hand, dry distillation of the (\pm)- or (-)-quaternary iodide at 150-

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200° and 30 mm furnishes (±)- or (+)-phellandrene along with α -terpinene.

Pyrolysis of the phenylurethane of (-)-trans-p-menth-2-en-1-ol (11b) affords (+)- α -phellandrene (1a).³⁷ Another interesting route to α -phellandrene consists of the simple dehydrobromination of 1:2-dibromo-p-menthane (13).³⁸⁻⁴¹

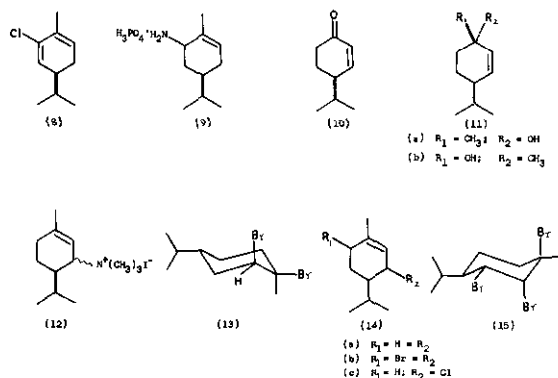
Reactions

Reduction. Reduction of α -phellandrene using sodium/amy alcohol combination effects selective absorption of one mole of hydrogen in Δ^5 -alkene bond resulting in p-menth-1-ene (14a).⁴² On the other hand, catalytic reduction under pressure in the presence of colloidal palladium furnishes a mixture of p-cymene and p-menthene.⁴²

Total hydrogenation leading apparently to a mixture of p-menthanes is accomplished by conducting the reaction over cobalt-nickel catalyst; from this conversion the heat of hydrogenation of the terpene has been roughly calculated.⁴³

Bromination. Work prior to 1948 on the bromination of α -phellandrene may be summarized as follows: Unlike β -phellandrene, the isomeric α -phellandrene refuses to yield a solid bromo derivative.^{44,45} In the presence of acetic acid, the terpene absorbs two bromine atoms, affording a dibromide (14b); further incorporation of bromine occurs with difficulty. Simultaneously, p-cymene seems to be released by loss of hydrogen bromide from the bromo compound. Treatment of the dibromide with alcoholic potash provides p-cymene and a fraction containing bromine.^{45a} More extensive study by Berry^{45b} apparently confirms these findings.

A recent significant contribution in this area is the isolation of tribromide (15), m.p. 82-84°.⁴⁶ However, attempts to obtain crystalline 1,2,3,6-tetrabromide from the terpene were unsuccessful.



Hydrochlorination. Theoretically, on hydrochlorination, α -phellandrene can generate the monohydrochlorides (15, 16, 17, and 18). Earlier investigations in this area are inconclusive.^{44,6,47,48}

Though the possibilities of converting α -phellandrene through its hydrochloride to valuable odor and taste chemicals were recognized as early as 1939,⁶ this was first exploited in a patent granted to Huggett and Porter in 1941,⁴⁹ covering the production of piperitone, thymol and menthol. The process consists of the initial formation of phellandrene chloride and then replacing the chlorine atom with an -OH radical by hydrolysis under displacement condition to form piperitol (19).⁴⁹ It therefore stands to reason that the hydrochloride involved is piperityl chloride (15).⁵⁰

The route to terpene alcohols from α -phellandrene developed by Bain, Booth and Klein⁵⁰ is more comprehensive. Reaction of α -phellandrene with hydrogen chloride yields piperityl chloride (15). Solvolysis under mild alkaline condition furnishes principally 2-menthene-1-ol (11) (in both *cis*- and *trans*- form), accompanied by small amounts of the allylmeric piperitol (19). Upon chromic acid oxidation, these alcohols afford piperitone (20) which can be converted into menthone and menthol by known methods.⁵⁰

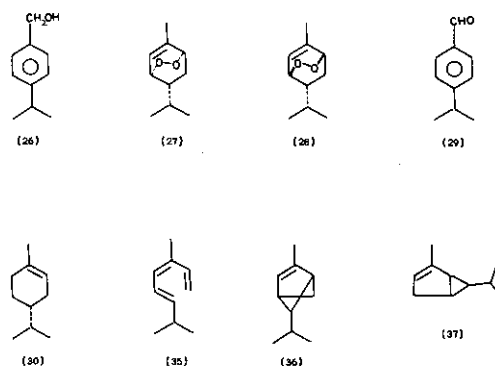
At this stage it is important to notice that the hydrocarbons recovered from the treatment of α -phellandrene hydrochloride contained β -phellandrene (21). Clearly then we have here a fascinating conversion of α -phellandrene to the hard-to-obtain β -isomer.⁵⁰

More recent work⁵¹ has confirmed the hydrochlorination route to the allylic alcohol (11) and further oxidation to piperitone (20). In addition, chromic acid oxidation of α -phellandrene hydrochloride to piperitone (20) has been claimed by Ohloff and Schade.⁵²

Oxidation. α -Phellandrene suffers rapid decomposition on standing in presence of air at ordinary temperature, registering a fall in optical rotatory power, and turns into a yellow, viscous and extremely sticky material.⁶ As a preservative, solid hydroquinone or another antioxidant is recommended, but the important precaution remains the use of tightly-fitting stoppers to exclude air.⁶ Exclusion of light is also recommended.

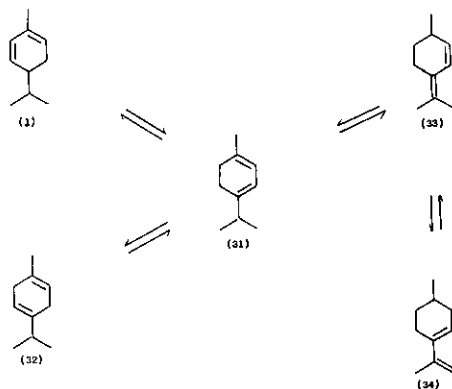
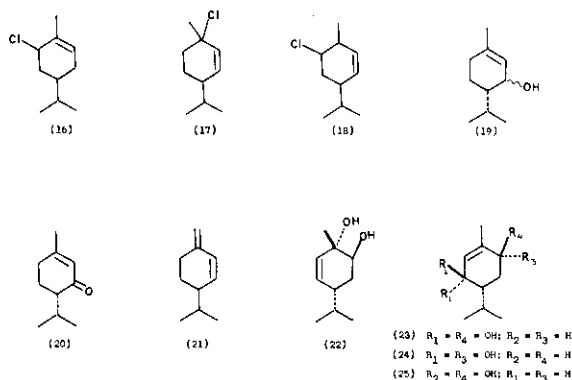
Four diols with melting points 54°, 112°, 149° and 168° are available by oxidation of α -phellandrene. These have been respectively assigned structures 22, 23, 24, and 25.⁵³⁻⁵⁸

Treatment of α -phellandrene with oxygen in the presence of organo-metallic complexes yields a mixture of cryptone (10) and cuminyl alcohol (26).⁵⁹ On the other hand, photosensitized oxidation of α -phellandrene furnishes both *exo*- and *endo*-3,6-epidoxyp-menth-1-ene (27 and 28).⁶⁰⁻⁶² Refluxing an ethanolic solution of α -phellandrene with selenium dioxide gives *p*-cymene and cumaldehyde (29).⁶³ A recent study has revealed that hydroboration-oxidation of α -phellandrene affords a multi-component mixture containing *p*-menth-1-ene (14) and *cis*- and *trans*- forms of carvotanacetol (30).^{64,65} Oxidation of α -phellandrene with Beckmann's chromic acid mixture has been investigated by Henry and Paget.⁶⁶



Isomerization and Dimerization. Under the influence of alcoholic sulfuric acid at room temperature or at boiling points, α -phellandrene is converted to α - and γ -terpinene (31 and 32) with concurrent formation of resins.⁶⁷ With syrupy phosphoric acid, the terpene yields the same isomers and a diterpene of unknown constitution.¹⁰

H⁺ catalyzed isomerization of α -phellandrene has been the subject of a recent comprehensive study.⁶⁸ The terpene, on vigorous stirring under nitrogen at 67° with twice its weight of 50% aq. sulphuric acid for 32 hr, gives an equilibrium

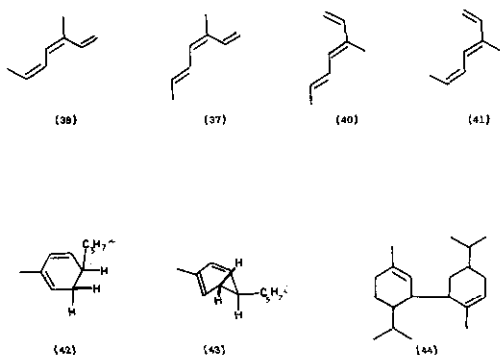


Isomerization of α -phellandrene

mixture of four isomers (31-34).

Upon ultraviolet irradiation, α -phellandrene reorganizes to a mixture of geometrical isomers of 3,7-dimethylocta-1,3,5-triene (35).⁶⁹ Extended irradiation of an ethereal solution of the terpene leads to a novel bicyclo isomer (36), now shown to be 6-isopropyl-2-methyl-bicyclo-(3.1.0)hexene-2 (37)^{70,71} formed via the triene (35).⁷¹

Unsensitized photolysis of α -phellandrene initially furnishes cis, cis- (38) and cis, trans- (39) 3,7-dimethylocta-1,3,5-trienes and these rearrange to the trans, trans- (40) and trans, cis- (41) isomers.⁷² Temperature dependance of the product ratios are in harmony with the postulate that the pseudoaxial isopropyl group conformer (42) is photoisomerized to the cis, cis-triene (38) while the pseudoequatorial conformer (43) is converted to the cis, trans-triene (39).



Naphthalene-photosensitized dimerization of α -phellandrene gives in 4.5:1:1 ratio (glc) three major products for which tentative structures have been assigned.⁷³

In presence of lithium naphthalene, α -phellandrene dimerizes to 44.⁷⁴

Finally Semmler and Jonas⁷⁵ have reported the polymerization of α -phellandrene by heating in a sealed tube to approximately 300°; a mixture of α -phellandrene and isoprene under similar conditions furnishes a sesquiterpene.^{75*}

Dehydrogenation and disproportionation

When heated with sulfur, α -phellandrene gives p-cymene.⁷⁶

(-)- α -Phellandrene, when refluxed in the presence of sodium sand and a small amount of freshly prepared benzyl-sodium as promoter, undergoes racemization accompanied by a rapid dehydrogenation to p-cymene.⁷⁷ The rate of dehydrogenation exceeds that of racemization by

*Because of the interest sesquiterpenes have received as important constituents of essential oils and as possible reaction-partners in syntheses, this somewhat neglected product deserves attention. Its chemical configuration should be elucidated, its sensory properties with regard to odor evaluated, and its possibilities to produce other aroma chemicals investigated. Another possibility would be to evaluate the reaction of isoprene with other terpenes under similar conditions (sealed tube—300°C).

an approximate factor of two. Semicyclic or exocyclic conjugated diene are not formed in the racemization process. These changes have been accommodated by a carbanion mechanism.⁷⁷

By heating α -phellandrene with a solution of N-sodioethylenediamine, $\text{H}_2\text{N}-\text{CH}_2\text{CH}_2\text{NH}_2$, p-cymene is obtained in a yield of approximately 75%.⁷⁸ With N-lithiotrimethylene diamine, $\text{H}_2\text{N}-\text{CH}_2\text{CH}_2\text{NHLi}$, conversion to p-cymene is considerably lower (approximately 40%).⁷⁸

With nickel catalyst, Dewar and Read have demonstrated the disproportionation of (-)- α -phellandrene to p-cymene and p-menthane in the approximate ratio 4:1.⁷⁹

Hitherto a neglected p-menthadiene, α -phellandrene at long last has found a worthy place as a raw material for chemical processing, leading to valuable products such as thymol, menthol and p-menthenyl alcohols. Further research on this terpene should open up routes to many other interesting and useful chemicals.

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