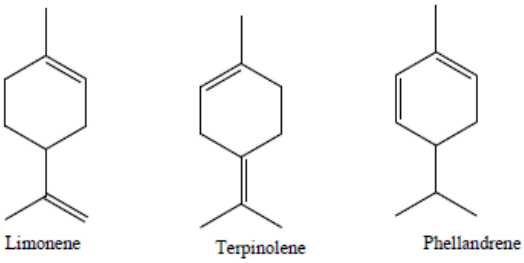
MONOCYLIC MONOTERPENOIDS

A. Hydrocarbons e.g Limonene, Terpinolene, α and β-phellandrene

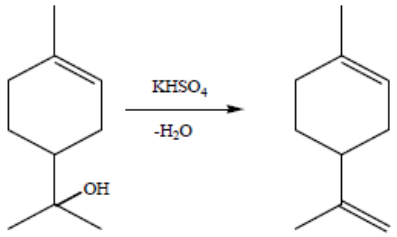


Limonene, $C_{10}H_{16}$

Occurrence: This is one of the most widely occuring monoterpenoids and exists in the form of (+)-limonene, (-)-limonene and (±)- limonene. The (+)-limonene occurs in citrus fruits peels (citrus oil) e.g orange , grapes etc. The (-)-limonene is common constituents of peppermint oil. The (±)- limonene is a common constituents of turpentine oil obtained from pinus species (pines).

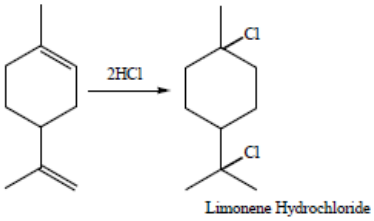
Preparation:

(+)- Limonene can be prepared by dehydrating (+)-α-terpineol with potassium hydrogen sulphate



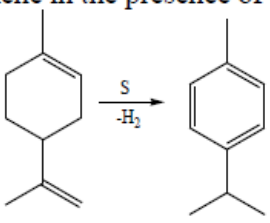
Chemical Reactions

1. Reaction with hydrogen chloride: (+)- or (-)- limonene adds on 2 molecules of HCl in the presence of moisture to form limonene dihydrochloride.

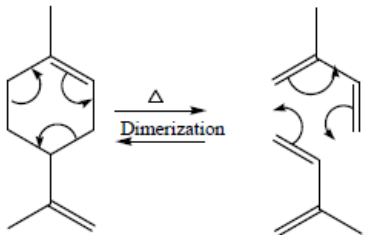


Limonene Hydrochloride

2. Limonene produces *p*-cymene in the presence of sulphur



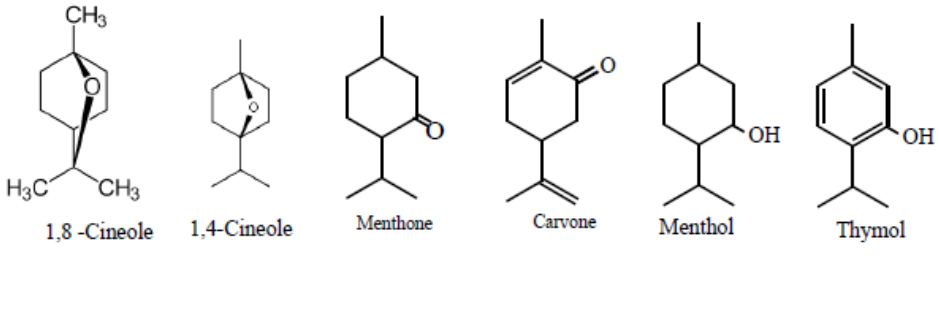
3. Pyrolysis: On pyrolysis, limonene undergoes reverse Diels Alder reaction to give 2 molecules of isoprene. The isoprene molecules could undergo Diels Alder reaction to form limonene



B. Oxygenated derivatives

Oxygenated derivatives can be classified into 4 classes based on the position of the oxygen. This classification is inevitably arbitrary and the interconversion between them are facile. These classes are:

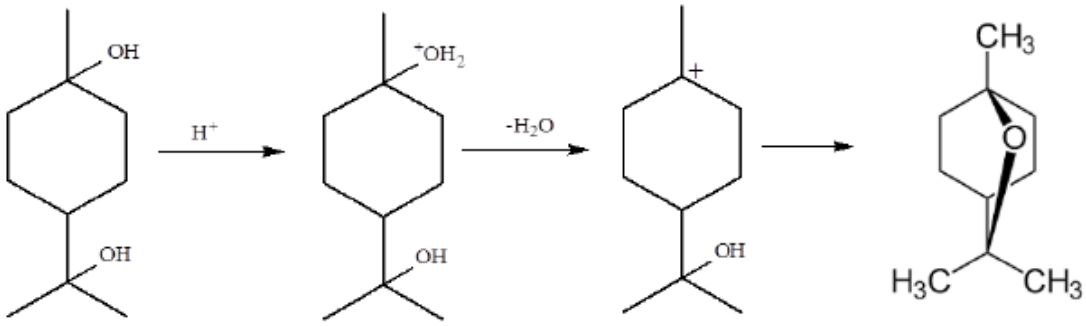
1. 1:8 Cineole group – oxygen at position 1 and/or 8 e.g. 1,8-Cineole
2. 1:4 Cineole group – oxygen at position 1 and 4 e.g 1,4-Cineole
3. Methone group – oxygen at position 3 or 5 e.g. Menthone,Menthol, Thymol
4. Carvomenthone group – oxygen at position 2 or 6 e.g. Carvone



1,8- Cineole, $C_{10}H_{18}O$

Occurrence: 1,8- Cineole is found in eucalyptus oil. It has a high milky smell and is used extensively in the preparation of inhaler (nose drop).

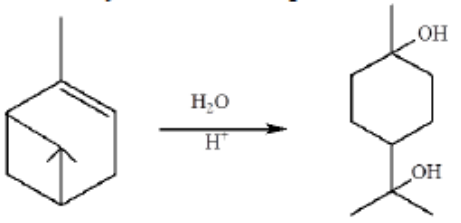
Synthesis: Dehydration of 1,8 – Terpins:



1,8 - Terpin

1,8- Cineole (Natural)

1,8- Terpin can be obtained from hydration of α-pinene

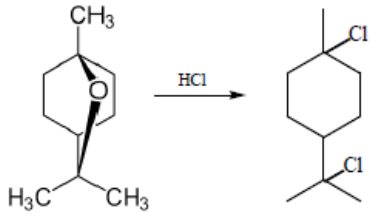


α-pinene 1,8 - Terpin

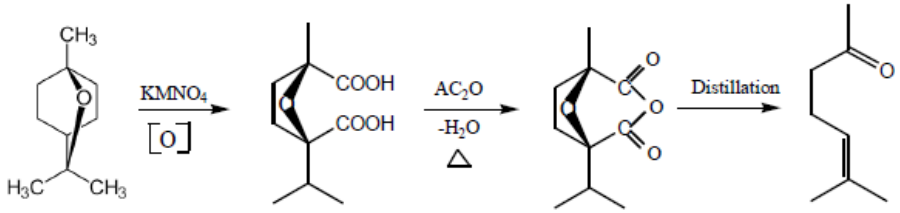
Reactions

Because 1,8 – Cineole is an ether, it is relatively unreactive but still undergoes some reactions

1. With HCl: it reacts with HCl to give limonene dihydrochloride

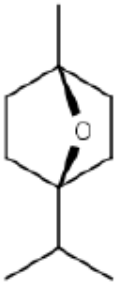


2. Oxidation: Vigorous action with $KMNO_4$ will yield a dicarboxylic acid (Cineolic acid), this when heated with acetic acid anhydride gives an anhydride. The anhydride when distilled at atmospheric pressure will form 6-methyl-5-heptenenone.



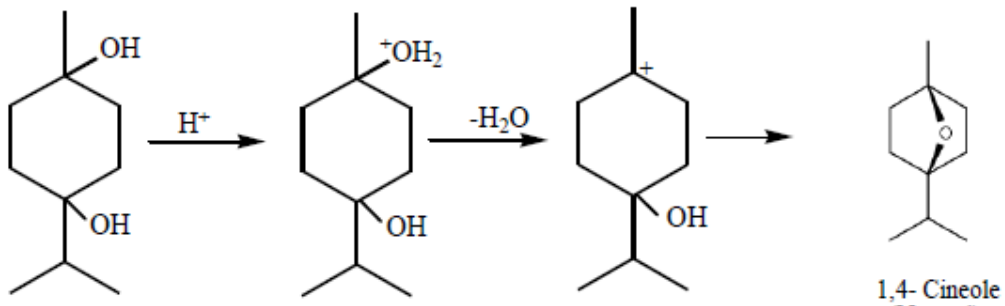
6-methyl-5-heptenenone

1,4-Cineole, $C_{10}H_{18}O$



Occurrence: It is found in the oil of cubeb (pepper)

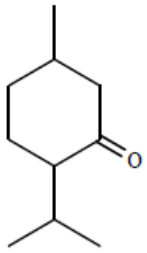
Synthesis: Dehydration of 1,4 -Terpins



1,4 - Terpin

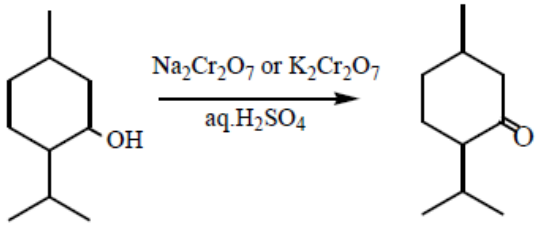
1,4- Cineole (Natural)

Menthone, $C_{10}H_{18}O$

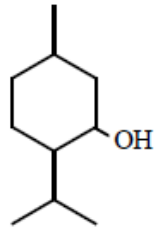


Occurrence: Menthone is a constituent of the essential oils of *pennyroyal*, *peppermint*, *Mentha arvensis*, *Pelargonium geraniums*, and others. Menthone is used in flavoring, perfume and cosmetics for its characteristic aromatic and minty odor.

Preparation: Oxidation of menthol with acidified dichromate



Menthol , $C_{10}H_{20}O$



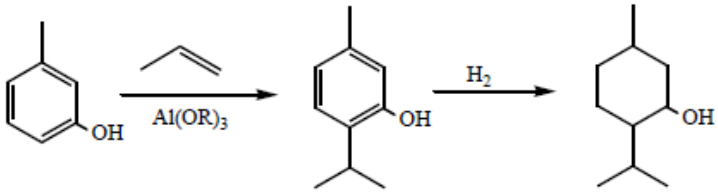
Menthol

Occurrence: It can be obtained from the oils of corn mint, peppermint or other mints

Uses: Menthol ability to chemically trigger the cold-sensitive TRPMS receptors in the skin is responsible for the well-known cooling sensation it provokes when inhaled, eaten or applied to the skin.

Preparation

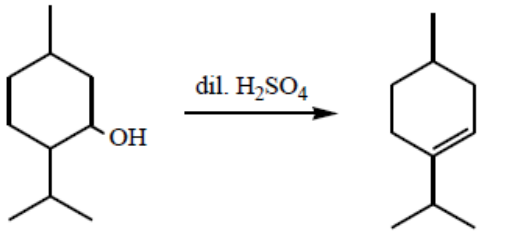
Haarmann-Reimer: Alkylation of m-cresol using propene followed by hydrogenation will yield menthol.



Reaction

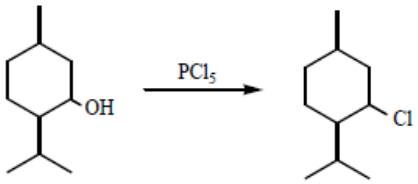
Menthol reacts in many ways like a normal secondary alcohol.

1. Oxidation: it is oxidised to menthone by oxidising agent such as chromic acid or dichromate
2. Dehydration: it is easily dehydrated to give 3-menthene

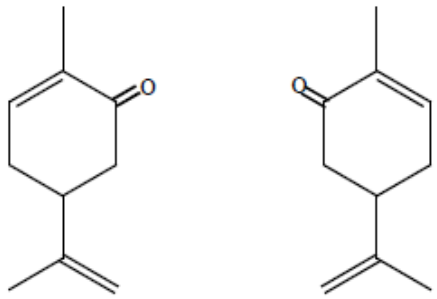


3-menthene

3. Menthol reacts with Phosphorous pentachloride (PCl_5) to give menthylchloride



<u>Carvone</u>, $C_{10}H_{14}O$

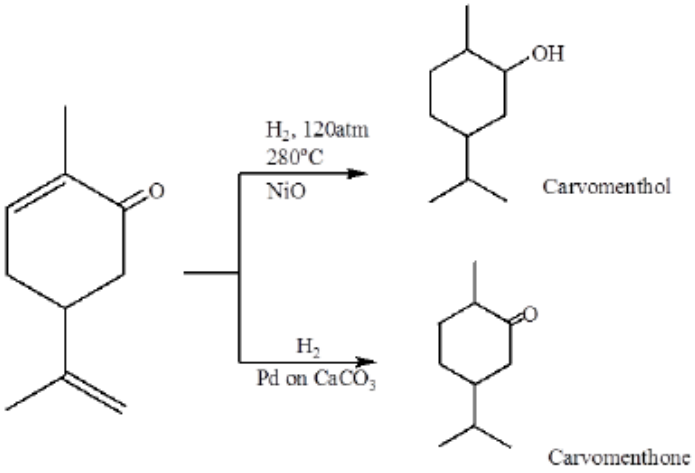


S – (+) –Carvone R – (-) -Carvone

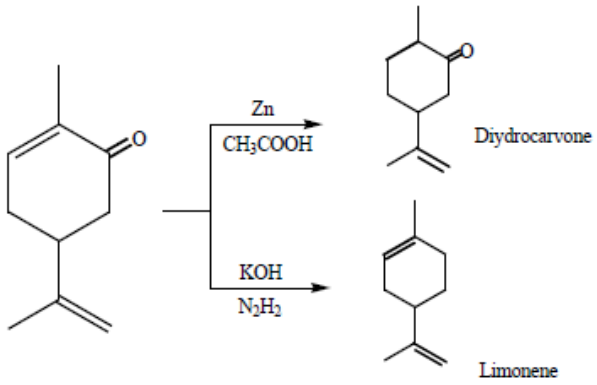
Occurrence: Carvone occurs in various essential oils e.g. Spearmint and Caraway oils.

Reactions

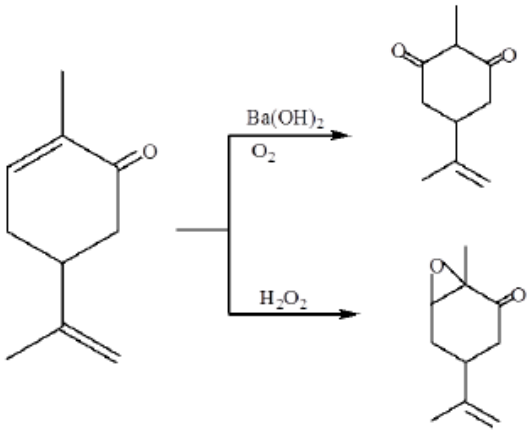
Catalytic Hydrogenation



2. Reduction



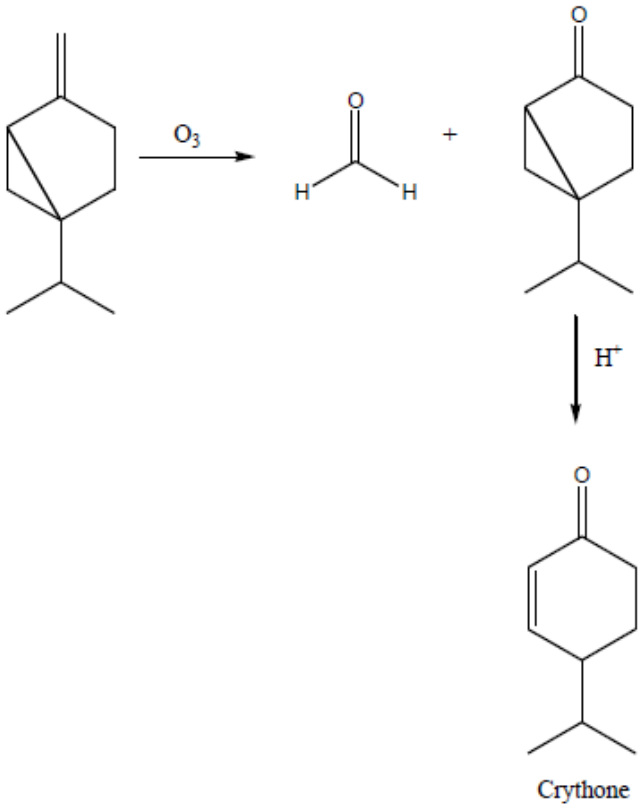
3. Oxidation



Reactions

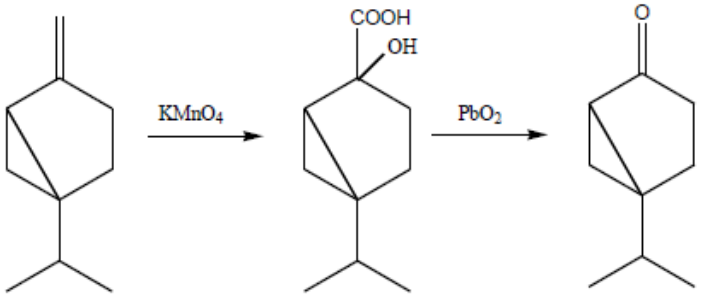
1. Oxidation

(a)



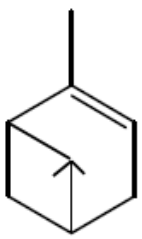
Crythone

(b)



Sabina ketone

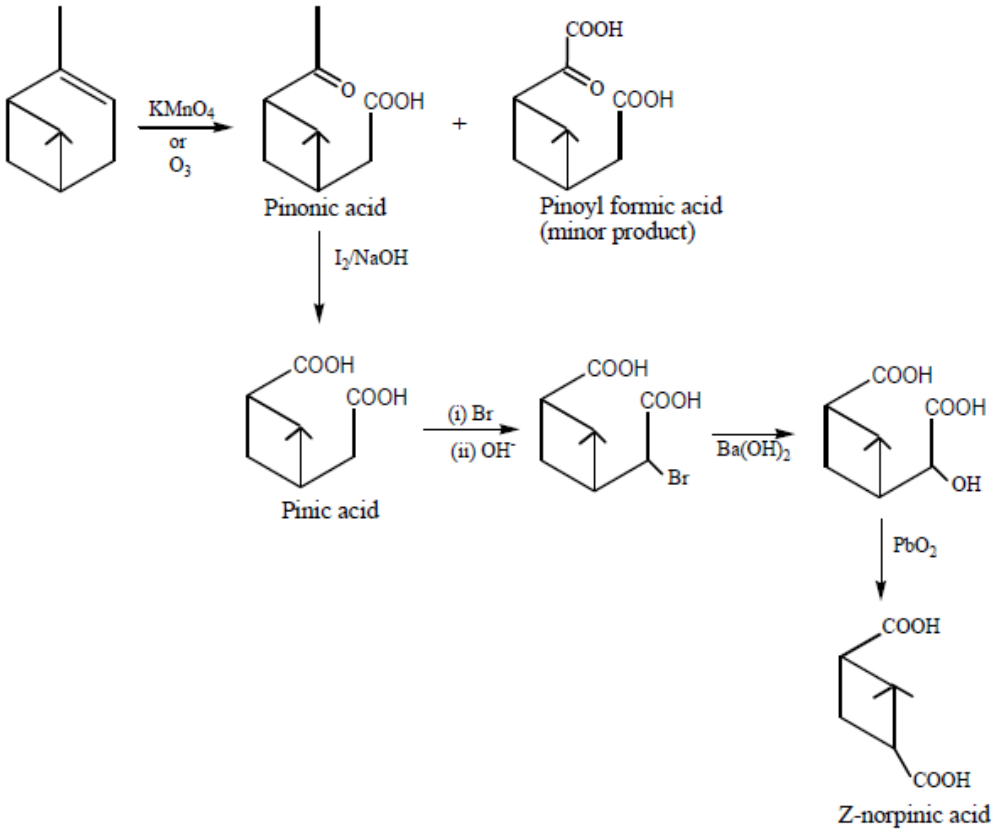
<u>α-Pinene</u>, $C_{10}H_{16}$



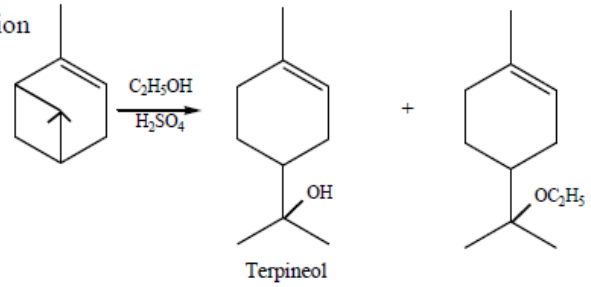
Occurrence: It occurs in both the (+) and (-) forms in turpentine oils.

Reactions

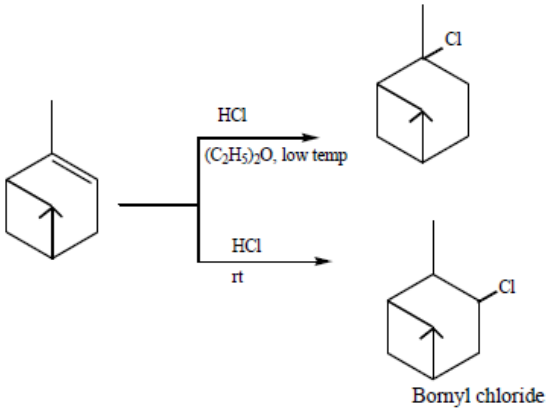
1. Oxidation



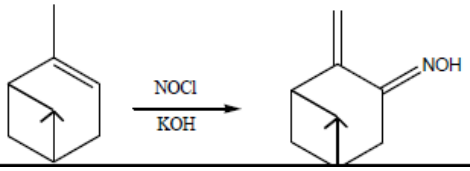
2. Rearrangement reaction



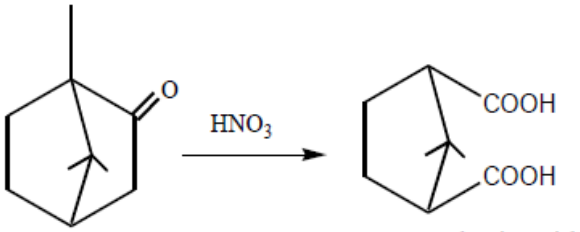
3. Reaction with HCl



4. Reaction with nitrosyl chloride followed by base leads to oxime



2. Oxidation: Camphor when oxidised with nitric acid yields a dicarboxlyic acid called camphoric acid.



Camphoric acid

3. Bromination