

B) synthesis and applications of perfumery

* Synthetic perfume -

Perfume may be defined as a mixture of pleasant smelling substances incorporated in a suitable solvent.

It is composed of three ingredients i.e. solvent or vehicle, fixative and odouriferous substances.

I. solvent or vehicle -

solvent require to keep the odouriferous substances in solution.

Good solvent must be volatile, inert and non irritant to human skin and almost colourless and odourless.

Highly refined ethanol mix with more or less water according to stability of oil is employed.

The solvent with its volatile nature carries the odouriferous substances to the cells of nose.

II. Fixative -

Generally perfume has two or more odouriferous substances and different volatility. In such cases more volatile fragment gives its odour first then the less volatile and so on.

In such perfumes it will give a series of impressions (odour) rather than desired fragrance.

To overcome such difficulty a fixative is added. "fixatives are substances of lower volatility than the perfume oil".

Their main function is to equilibrate the rate of evaporation of the various odouriferous constituents of a perfume by retarding or increasing their volatilities.

All fixatives are classified into following four

Groups.

- (a) Animal fixative
- (b) Resinous fixative
- (c) Essential oil fixative
- (d) synthetic fixative.

(a) Animal fixatives:

Name of oil	Source	Remark	component
Musk	Sometimes at the hepatic glands of the male musk deer	Most useful animal fixative.	Muscone, (cyclic ketone)
Musk zibuta	Gland at the musk rat	latest animal fixatives	Macrocyclic ketones.

(b) Resinous fixatives

These are normal or pathological exudates of certain plants.

They are more important historically rather than commercially.

Their various important resinous fixatives are given below.

- (i) hard resin - e.g. Benzoin
 - (ii) softer resin - e.g. Myrrh and Labdanum
 - (iii) moderately soft resin - e.g. Peru balsam, Tolu balsam
 - (iv) oil resin - e.g. Terpenoids.
- Extracts from resin - e.g. Ambrein.

(c) Essential oil fixatives -

certain essential oils are used for their

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fixatives as well as odouriferous properties.
e.g. clary sage, yerviver and sandel wood, Patchouli

The boiling points of these oil are in the range of $235-290^{\circ}\text{C}$ a higher range than normal essential oil.

(d) Synthetic fixatives -

These are used as only fixatives to replace some of the animal and plant fixatives.

They are high boiling odourless esters.

e.g. Glyceryl diacetate (B.P. 259°C), ethyl phthalate (B.P. 213°C) and benzyl benzoate (B.P. 323°C).

As those which function as a fixatives as well as odouriferous substance i.e. in order to their fixative properties they also impart their fragrance to the perfume in which they are used.

e.g. Amyl benzoate, phenyl ethyl.

1 2-phenyl ethanol -

It is one of the most widely used aromatic perfumery compounds because of its mild, pleasant and persistent rose odour.

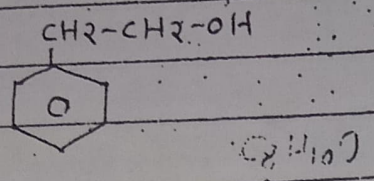
It is frequently used in rose and many other types of perfume compositions.

Its stability towards alkali makes it a specially suitable for imparting perfume to various types of soaps and cosmetics.

It occurs in the volatile oils of rose, orange flowers and others.

There are large no. of methods for synthesis of phenyl ethyl alcohol. The important commercial methods are given below.

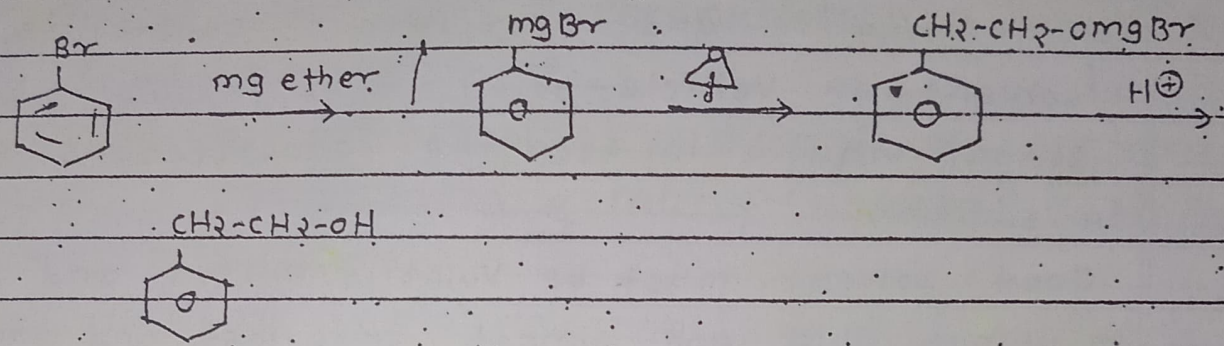
Structure-



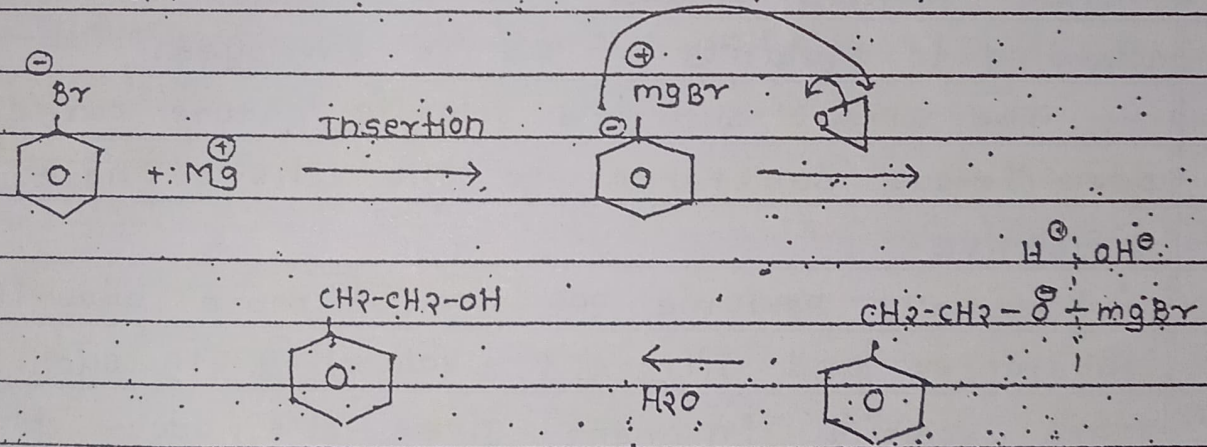
Methods-

I. By grignard reagent - phenyl magnesium bromide and ethylene oxide.

Reaction-

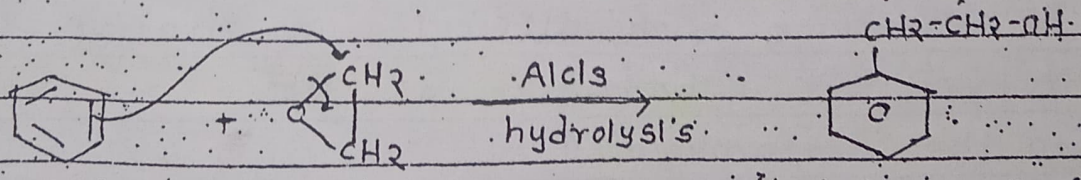


Mechanism-



II. By Friedel craft reaction - betⁿ benzene and ethylene oxide in presence of AlCl₃.

Reaction-



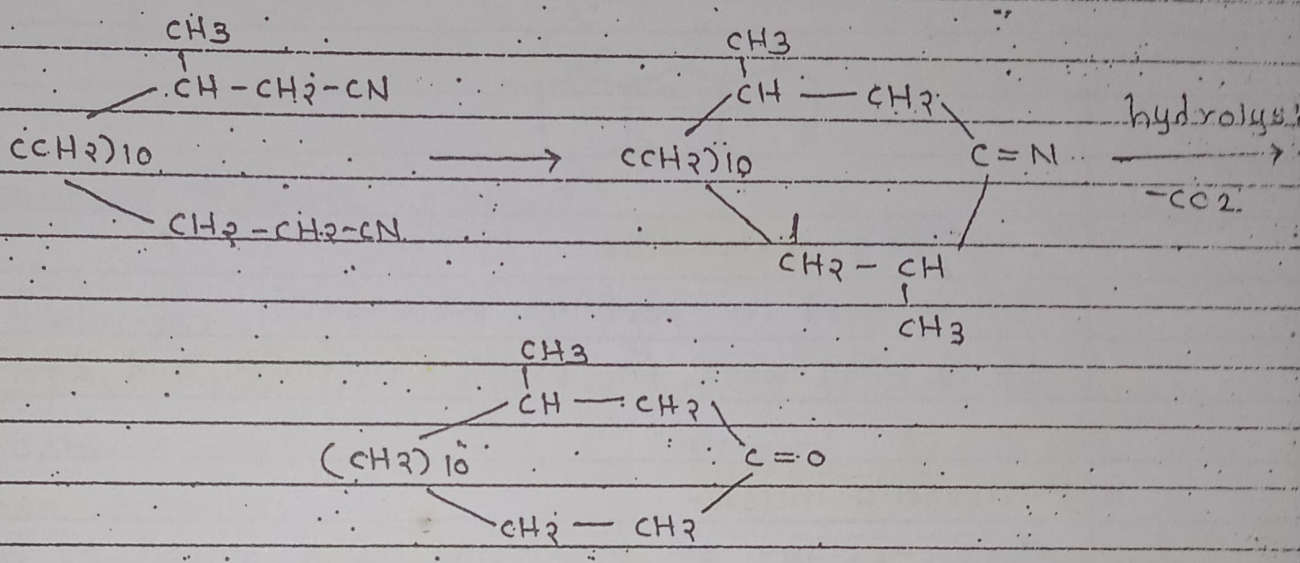
several esters of phenyl ethyl alcohol are also used in perfume.

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2. Myscone

Myscone is the active principle of tinctin. Musk like civetone, it is also a macrocyclic ketone.

It gives outstanding results in face water composition. It synthesizes as follows:



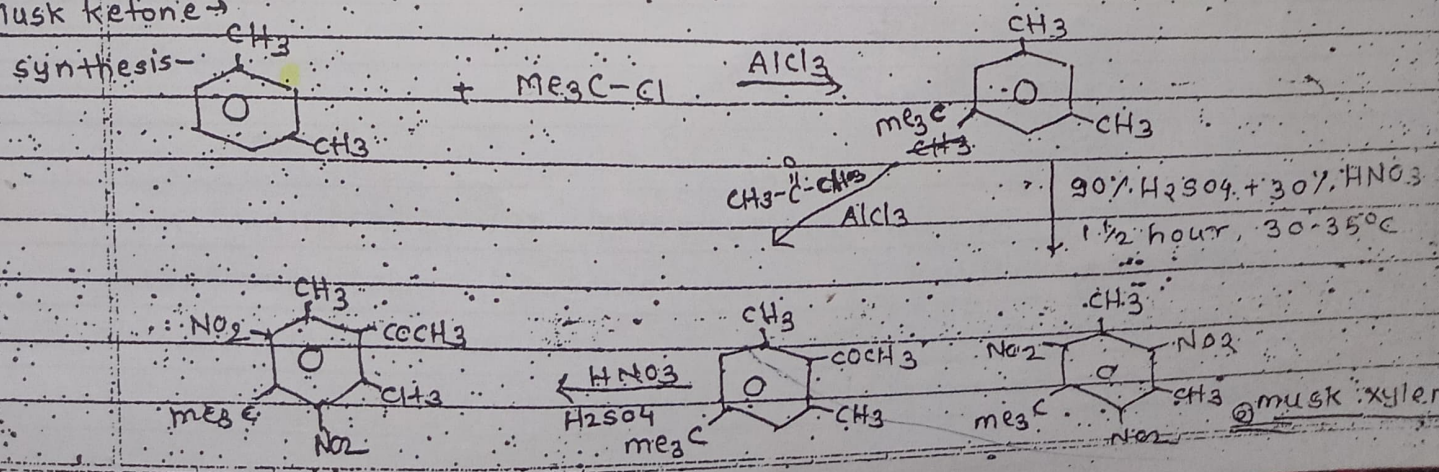
③ Synthetic / Artificial nitro musk

Various synthetic compounds are found in process the musk like odour and their use in perfumery is so frequent that nearly all perfumes have some amount of nitro musk.

The various nitro musk are musk xylene, musk ambrette, musk xylol and musk ketone.

These artificial musk are synthesized from meta-xylene.

1. Musk ketone synthesis

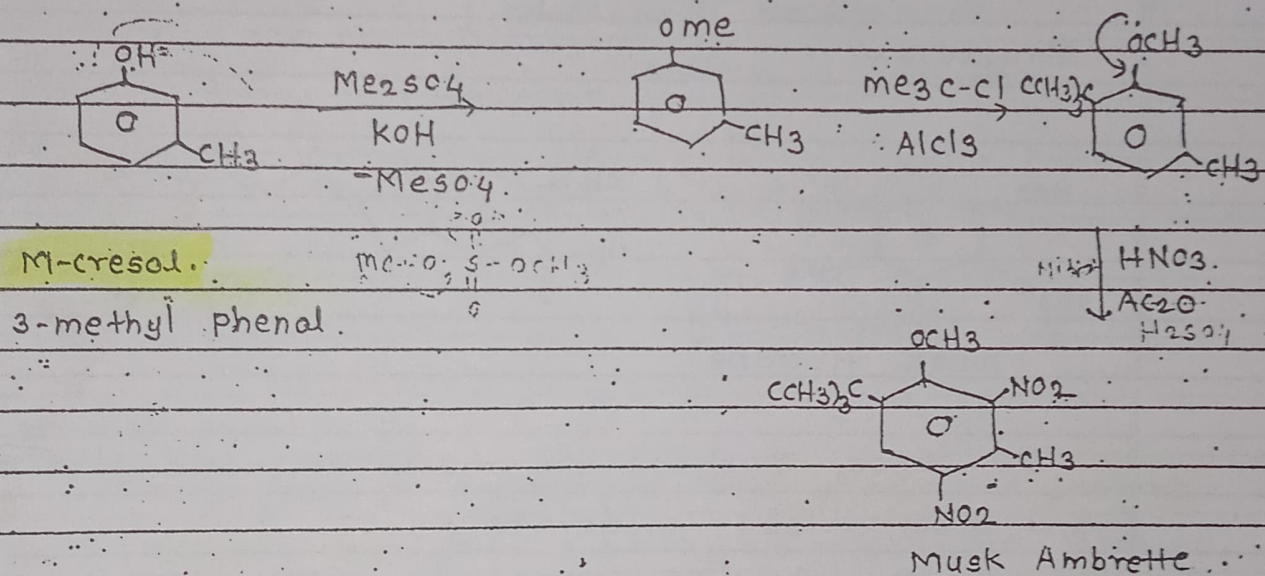


Musk xylene has a powerful natural musk like odour and it is extensively used in perfume synthesis while the musk ketone is the consist. in odour to the natural musk.

Musk xylene is an economical sweetener for floral soap and detergent.

Generally it accounts that nearly more than half of the nitro musks used in perfume industries.

① Musk Ambrette-

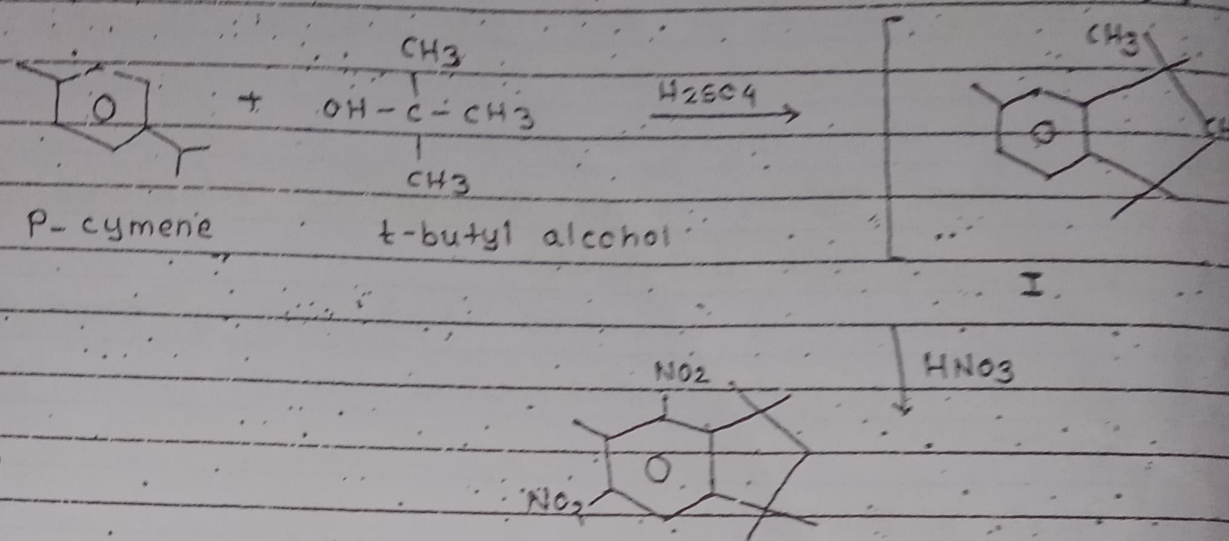


Among all the nitro-musk, musk ambrette is the strongest in odour and it is widely used in soaps.

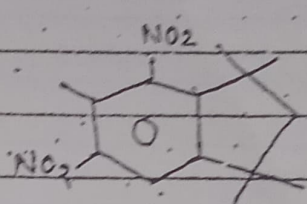
The most serious disadvantage of these musk is shows discolouring characteristics in presence of heat or light.

② Muskene-

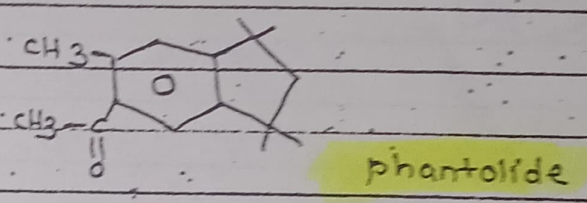
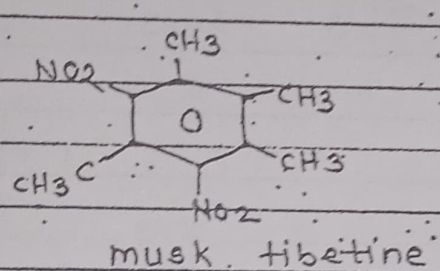
It is prepared from p-cymene in presence of tertiary butyl alcohol. It form intermediate (I), then it carried out nitration in presence of HNO_3 and H_2SO_4 to form Muskene.



HNO_3



Structure -



Since muskene has musk ambrette like odour and discolourless moderately. It is extensively used to obtain the musk ambrette odour.

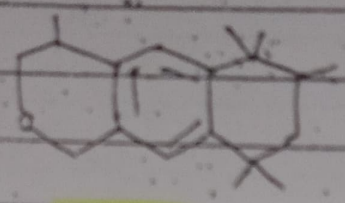
Synthetic musk known as white musk in perfume industry.

They are divided into following classes.

- I. Aromatic bito musk
- II. polycyclic musk
- III. Macrocyclic musk
- IV. Acyclic musk

II Polycyclic musk -

It is an artificial musk that contain more than one ring in the molecular structure



eg Galaxolide

It is used in perfume preparation

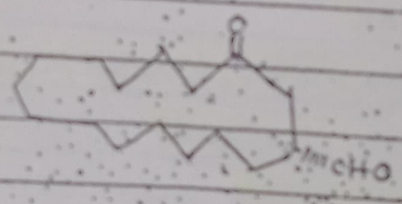
It is also used in fabric softeners and detergent

III Macrocylic musk -

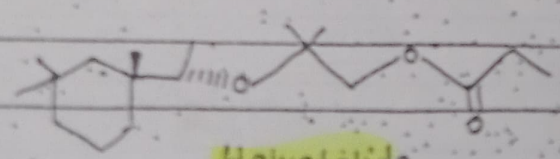
It is a class of artificial musk, which is composed of more than 6 carbon

These musk are extracted from plants consist of large ring lactones.

All animal derived macrocylic musk are ketones.



IV Acyclic musk



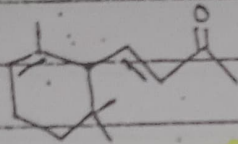
Helvetolide

It is known as cycloalkyl ester or linear musk are relatively a novel class of musk compound.

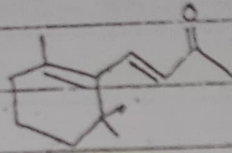
These are different in structure than various musk or previous musk and these is

Inone -

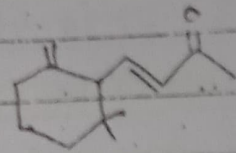
Structure -



α -Inone



β -Inone



γ -Inone

chemical formula - $C_{13}H_{20}O$.

Introduction -

The Inone are series of closely related chemicals substance that are part of compound known as rose ketones.

Inones are aroma compounds found in a variety of essential oil including rose oil.

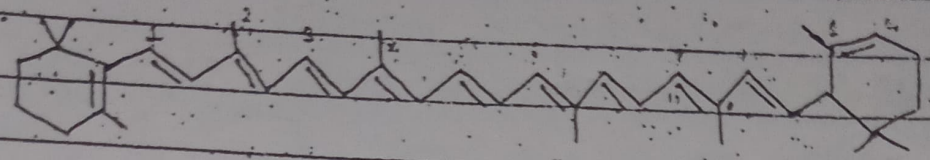
It is an important fragrance chemical used in perfumery.

The ionone are derived from the degradation of carotenoid.

The combination of α -ionone and β -ionone is characteristics of scent of violet and used with other component in perfumery and flavouring to recreate their scent.

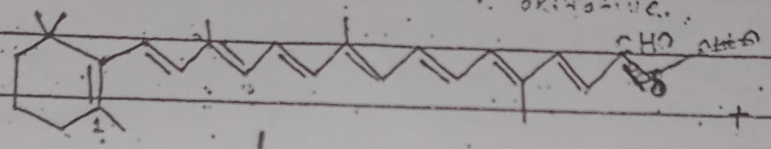
Biosynthesis -

Carotenoid are the precursor of important fragrance compound in several flowers.



α -carotene

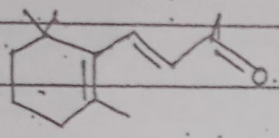
carotenoid deoxygenase



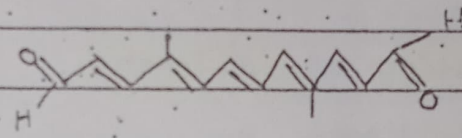
10'-apo β 10' carotenal

carotenoid deoxygenase

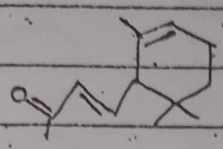
cleavage 2



β -ionone



C₁₄-dialdehyde



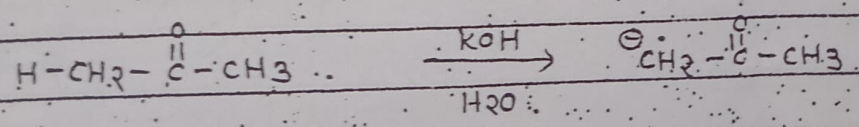
α -ionone

Organic synthesis:-

Inone can be synthesized from citral and acetone with calcium oxide as a basic heterogeneous catalyst and serves as an example of an aldol condensation followed by a rearrangement reaction.

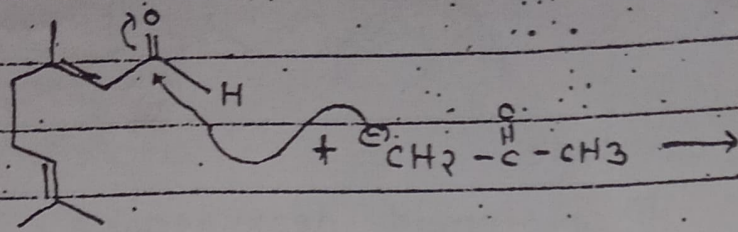
Step I -

Formation of carbanion-

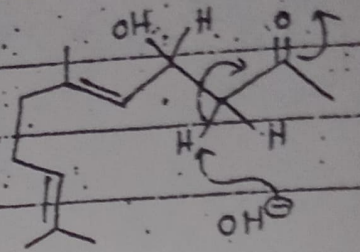


Step II -

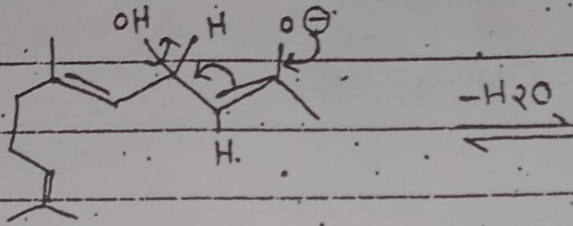
Formation of pseudoionone



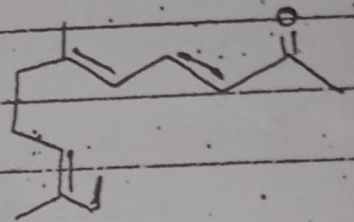
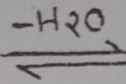
citral



keto enol



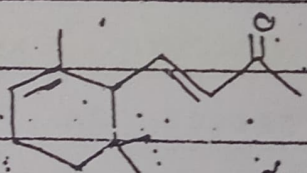
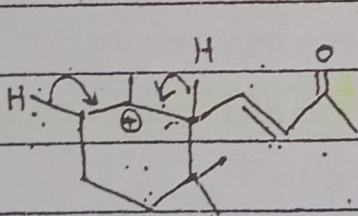
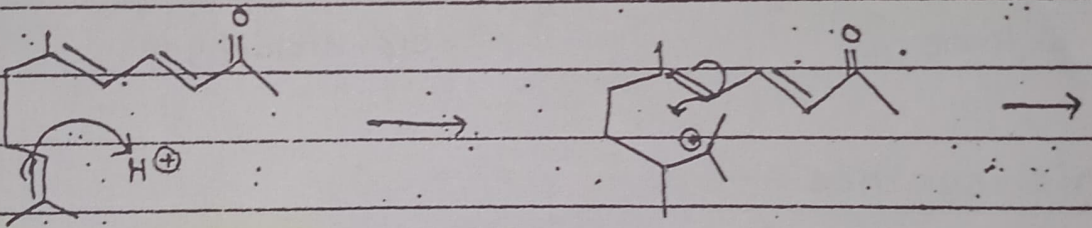
enol



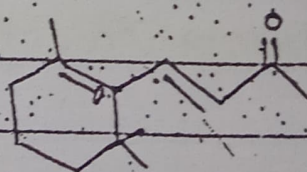
Pseudoionone

step - III -

Formation of α -ionone



α -ionone



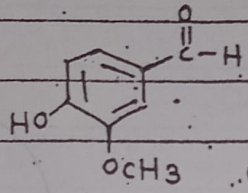
β -ionone

Vanillin -

Vanillin is a naturally occurring aromatic compound in vanilla beans.

It is used in a wide range of areas from flavoring, medicine and perfume.

Structure -

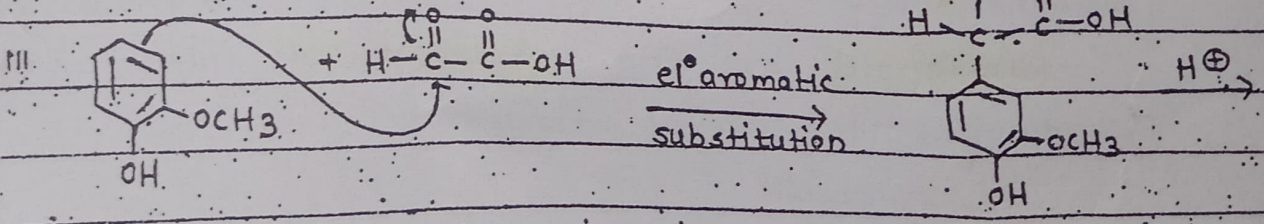
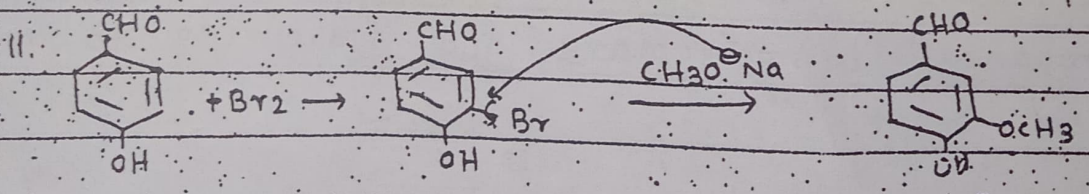
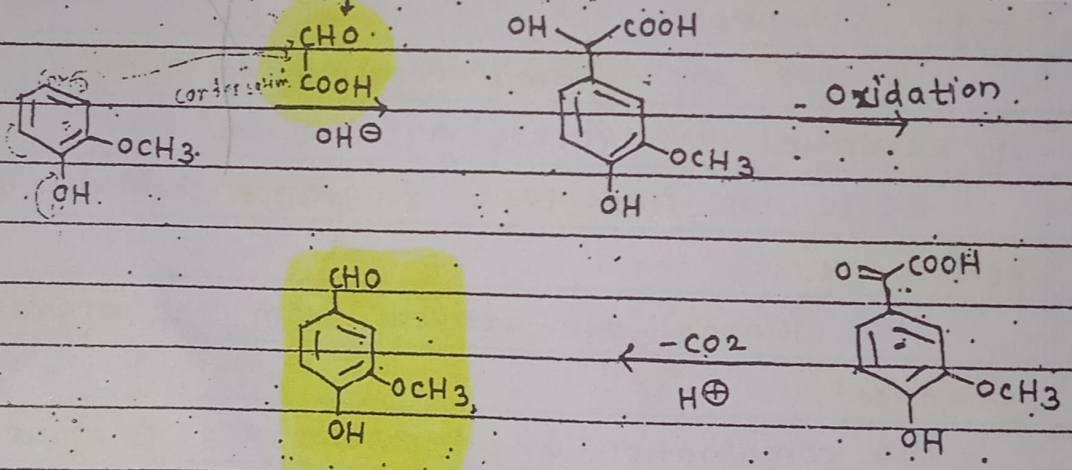


(4 hydroxy 3-methoxy benzaldehyde)

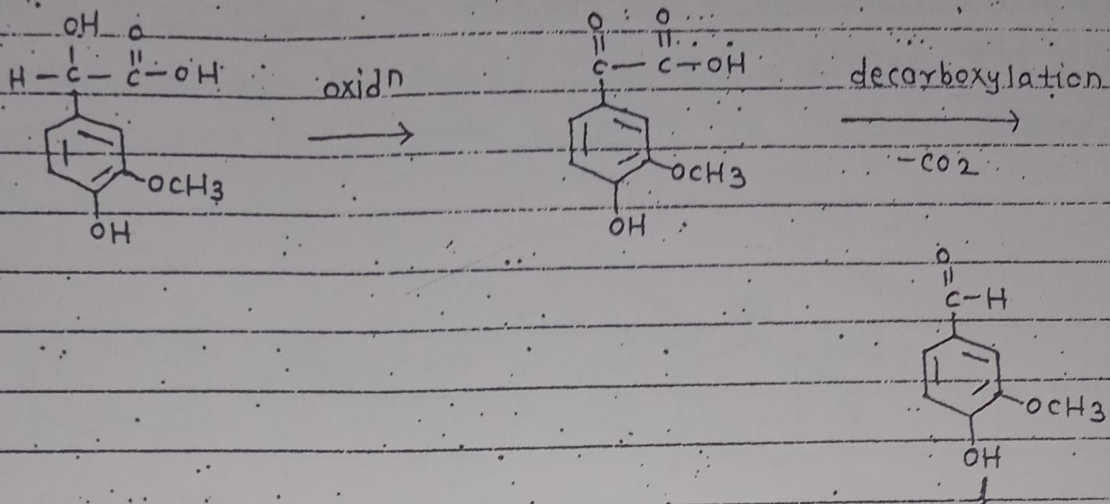
Molecular Formula - $C_8H_8O_3$.

Synthesis -

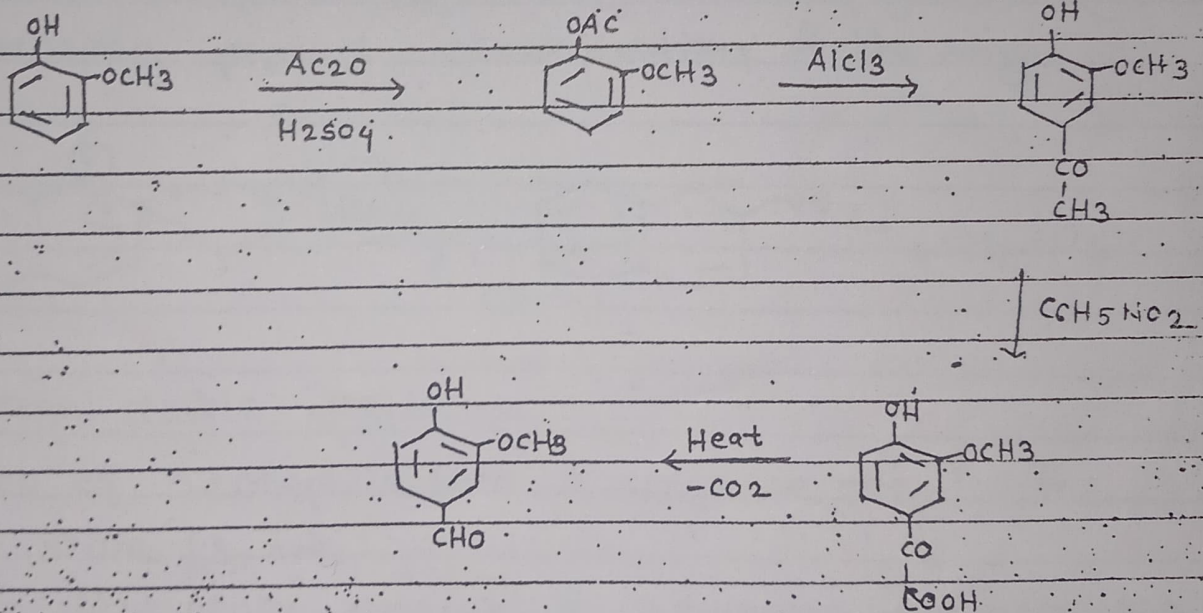
I. From guaiacol - glyoxylic acid.



(14)



III.



Applications of Vaniline-

Vanillin is a chemical compound widely used as perfume in food production.

As a perfume, Vanillin can be used in a wide variety of industries including food production, beverage, pharmaceutical, cosmetics, agriculture / animal feed, and various other industries.

Vanillin in food production.

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Page No.

Date

- Vanillin used as perfume in food production
As flavor changer - in chocolate, candies, biscuits, instant noodles and bread to improve flavour.
- Vanillin used as flavor changer in beverage.
as flavor changer - in ice-cream to improve flavor.
- Vanillin in pharmaceuticals. (intermediate)
as intermediate - in manufacturing of medicine.
- Vanillin used as fragrance in cosmetics.
As fragrance - in commercial perfume to endue milk flavour.
Vanilla extract used as flavoring agent in food

* Food Flavours -

Flavour is the sensory impression of a food or other substance, and is determined mainly by the chemical ~~es~~ senses of taste and smell.

The taste of food is limited to sweet, sour, Umami bitter, salty, and other basic tastes.

The smells of a food are potentially limitless.