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Research Article

Economic Ways of Isomerisation of Tert Allylic Alcohol by using Alumina Modified with Consumable Acid.

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ABSTRACT

Isomerisation of Geraniol-Nerol to linalool and vice versa has been mentioned in the various literature and patents. However, an important factor is to make it economically more viable that can be scaled up to commercial levels. Many transition metal catalysts are known to convert linalool to geraniol-Nerol and vice versa but the main problem is cost of the catalyst, its recovery and its reusability. The current method ,mentioned in the paper, involves the use of a cheaper organic acid i.e ascorbic acid coupled with alumina catalyst which is low in cost, quantity required is very less, and also gives good conversion with minimum side products.

Keywords: alumina, minimum, economically

INTRODUCTION:

In Terpene chemistry, geraniol-nerol and Linalool find wide application in the various fragrance industries as they appear to have a rosy smell (Geraniol-Nerol) and floral spicy woody (Linalool) note. Isomerisation of geraniol nerol to linalool and vice versa is one of the most studied reactions as it leads to the conversion of one fragrance molecule to another . Various catalysts have been studied over years which involve Tungsten, Vanadium and other metals. The major problem with the use of these catalysts is that their preparation is difficult, and next difficulty is scalability and commercial use.

The mechanism by which the isomerisation takes place is generally explained by bond formation between the electron deficient metal with ,both the electron rich oxygen atom and the allylic double bond which further involves the simultaneous migration of hydroxyl group and double bonds. The reaction stops at an equilibrium stage which may depend upon the type of catalyst used and other reaction conditions.

The main challenge in forming the products is minimising the side products and also reducing polymerisation. As we all know that linalool is a tertiary alcohol which in the presence of acidic medium can easily undergo dehydration and form undesired products which further can cause problem both in terms of separation and also loss of quality raw materials. So determining the conditions which can give good conversion with minimum side products(which are separable) is the most important requirement.

The method mentioned in the paper deals with the use of acidic alumina coupled with a weak organic acid like ascorbic acid at the temp of 140-260 C and without the use of solvent or any other material. The main idea behind using alumina and ascorbic acid is to obtain the desired selective acidity which can help isomerisation and also minimise the impurity profile. Small quantity of water is also required for the reaction as it can mix ascorbic acid with alumina.

RESULTS AND DISCUSSION: -

The method of allylic alcohol isomerisation has been known for a long time in which various metal catalysts have been used. The basic mechanism remains the same i.e. simultaneous migration of the allylic double bond and the hydroxyl group. The extent of migration depends on the various factors like the catalyst used, structure of the molecule and temperature. A slight change in the condition can convert everything into either hydrocarbon or polymer. This is mainly because of the acidic medium which can cause various side products due to various possible rearrangements. So careful fine tuning is required ,as both hydrocarbon formation or polymerisation is possible.

It has been observed that the catalyst mentioned in the literature (1-7) shows the use of vanadium, Tungsten etc metals in isomerism. Here in one patent WO20030488091A2 transition metal catalyst used is tungstic acid which is the heterogeneous metal catalyst and which binds at one site of the allylic double bond and the other end to the oxygen atom of the hydroxyl group. This results in isomerisation.

The process mentioned in the paper basically uses aluminum oxide as a catalyst to form the stable intermediate. The basis of formation of stable intermediate is due to the formation of a bond between the electron deficient aluminium oxide with both electron rich double bond and hydroxyl group. With the temporary transfer of electrons from the double bonds to the aluminium oxide and then from the aluminium oxide to the election deficient centre this type of rearrangement is achieved..

The other rearrangements are also possible which involves transfer of electrons from the metal centre to the lower double bonds and thus forming cyclised products .With further dehydration can cause a large number of unsaturated and saturated hydrocarbons(mentioned in Scheme1) .As with the saturated impurities there are not much reaction possible ie they are unreactive but in case of the unsaturated impurities, in acidic medium, can rapidly lead to polymerisation and residue formation. So reaction conditions must be carefully set.

The following scheme shows various possible by-products that can form in the reaction

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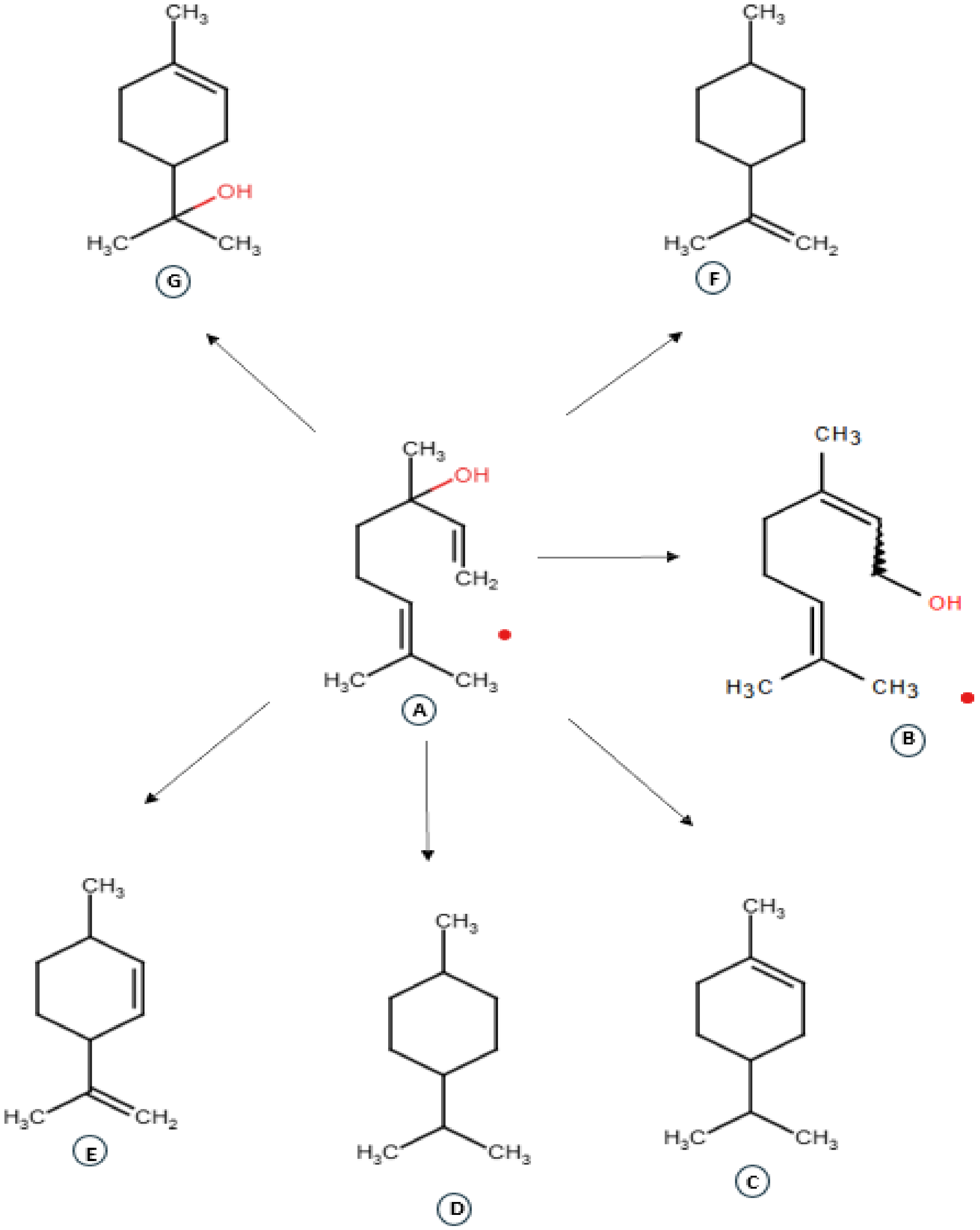

Scheme 1:

The scheme 1 shows the probable reaction products and also its by-products

Variations of temperature Vs products formed are studied while keeping the quantity of the catalyst (Alumina, Ascorbic acid and Water) and Raw material(linalool) constant.

The below table shows the Variations of temperature Vs products

Sr No	Linalool (mg)	Alumina (mg)	Ascorbic acid(mg)	water (mg)	Digestion. Time (Hrs)	Digestion. Temp (oC)
1	100	1	1	10	5	160
2	100	1	1	10	5	180
3	100	1	1	10	5	200
4	100	1	1	10	5	220

Table 1.1a

GC Conversion of the above reaction are as follows:

Sr No	Linalool (%) (A)	Geraniol (%) (B)	Nerol (%) (B)	Dipentene (%) (E)	Limonene (%) (F)	Terpineol (%) (G)	Others (%)(C,D)
1	60	5	2	3	8	10	12
2	50	7	6	4	4	7	12
3	30	8	7	5	3	2	45
4	10	7	6	13	10	15	39

Table 1.1b

From the above table 1.1a,1.1b it clearly indicates that with increase in temperature the impurity profile (side product) also increases.This indicates that the reaction is temperature sensitive.

Variation in catalyst quantity Vs the products formed are studied while keeping the temperature, linalool constant.

The following table shows the Variation in catalyst quantity Vs the products

Sr No	Linalool (mg)	Alumina (mg)	Ascorbic acid(mg)	water(mg)	Digestion. Time (Hrs)	Digestion. Temp (oC)
1	100	1	2	10	5	160
2	100	2	4	10	5	160
3	100	3	6	10	5	160

4	100	4	8	10	5	160

Table 1.2a

GC Conversion of the above reaction are as follows:

Sr No	Linalool (%) (A)	Geraniol (%) (B)	Nerol (%) (B)	Dipentene (%) (E)	Limonene (%) (F)	Terpineol (%) (G)	Others (%)(C,D)
1	60	5	2	3	8	10	12
2	70	7	6	4	4	7	2
3	75	8	7	1	1	2	6
4	72	7	6	2	1	1	11

Table 1.2b

From the above Table 1.1a,1.1b,1.2a and Table 1.2b it is clear that by changing the catalyst percentage and the temperature we can achieve good conversion with a lesser amount of byproducts.

The main problem with the acid catalyst i.e.combination of ascorbic acid,water and alumina, is that when the conversion goes above 20%, high boilers start forming which indicates that the conversion cannot go above 20%. Thus, the reaction thus stops at an equilibrium ratio which indicates that with this acid catalyst i.e.combination of ascorbic acid,water and alumina 100% conversion cannot be achieved. Due to the incomplete isomerisation, the reaction requires fractional distillation to get the pure products.

The temperature at which the isomerisation takes place is usually high i.e. above 150 C. This indicates that the isomerisation requires high temperature, but it is observed that when the temperature above 200 C the impurity starts forming. So, the preferable temperature is in the range of 140 and below 200.Thus it is a thermal driven rearrangement.

Here in this reaction, which unlike other processes doesn’t require tedious work up for catalyst removal. The reaction mixture can simply be filtered and then the remaining raw materials can be distilled. The flashed material can then be fractionated and the required isomers with desired purity can be Obtained..

Experimental section:

Example 1:

Charge 100 mg of linalool (purity 99% by G.C) with about 1mg alumina ,10mg water and 2 mg ascorbic acid. Allow the reaction mixture to stir for 2 -5 hrs. Raise the temperature to 150-180 C with the help of a heating mantle. Maintain it for 3-4 hours and monitor the reaction. After 4 hrs the conversion obtained was 15% Geraniol-

Nerol, 76% unreacted start and 9 % others (The others also includes the LB, HB).The percentage ratio of geraniol-Nerol obtained is (45-55%).

Example 2:

Charge 100 mg of linalool (purity 80% by G.C the other impurity) with about 1mg alumina ,10mg water and 2 mg ascorbic acid. Allow the reaction mixture to stir for 2 -5 hrs. Raise the temperature to 150-180 C with the help of a heating mantle. Maintain it for 3-4 hours and monitor the reaction. After 4 hrs the conversion obtained was 10% Geraniol-Nerol, 60% unreacted start and 10 % others (The others also includes the LB, HB).The percentage ratio of geraniol-Nerol obtained is (45-55%).

Example 3:

Charge 100 mg of linalool (purity 50% by G.C the other impurity) with about 1mg alumina ,10mg water and 2 mg ascorbic acid. Allow the reaction mixture to stir for 2 -5 hrs. Raise the temperature to 150-180 C with the help of a heating mantle. Maintain it for 3-4 hours and monitor the reaction. After 4 hrs the conversion obtained was 8% Geraniol-Nerol, 35% unreacted start and 7 % others (The others also includes the LB, HB).The percentage ratio of geraniol-Nerol obtained is (45-55%).

INSTRUMENTAL SECTION:-

The instruments required for the analysis is

1) GC 2014 (Make: Shimadzu).

2) HPLC (Make:Waters).

3) Distillation assembly along with other glassware.

4) GC MS (Make: Shimadzu)

CONCLUSION:-

Various reactions are known for the bringing the conversions but the main idea behind the reaction conditions mentioned in this paper is without the use of the toxic chemicals, less complicated and without the effluents.

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