Nanotechnology Perceptions
ISSN 1660-6795
www.nano-ntp.com

Studies of the Copper-Based Catalyst on the Allylic Reductions and its Selectivity Improvement When Applied to Terpenes

Rohan Kunder, Jayshree Parikh

Department of Chemistry, JJTU University, Vidyanagari, Jhunjhunu, India
Email: rohanjkunder@gmail.com

Studies of the copper-based catalyst on the allylic reduction are studied to the limited extent especially when there are other double bonds involved. Copper based catalyst shows a remarkable selectivity in not only minimizing the side products but easy separations if once formed. Various terpenes can be converted to valuable products by using copper catalyst with suitable modifiers.

1. Introduction

Terpenes are used in the variety of flavors and fragrances in various proportions. Synthesis of Terpenes in a cost effective and greener way has become more important and essential, as demand of terpenes in various fragrances and flavors formulations has increased globally. Citronellol is widely used in various fragrances, mosquito repellents and other formulations. Synthesis of citronellol by both cost effective way and economical ways has become increasingly important. The current process involves the use of the various catalyst and conditions are Rh- and Ru-based catalysts are used where Noyori Bs BINAP ligands are used [5] . When about the heterogeneous catalyst, uses of Pt /Pt oxide and Ni [6] while some papers mention catalytic systems such as Pt with zeolite[7] Pt/Al_2O_3 used with organic Acids,[8] Ni with alkali hydroxides [9] Raney Ni with alkaline metal hydroxides [10]

The above-mentioned paper /patents have the following limitations

1) The byproduct of reduction reactions ie Dimethyl octanol is formed which creates problems in distillation and for the generation of pure citronellol becomes a tedious task.

2)The use of costly catalysts such as Ruthenium, rhodium, platinum becomes commercially difficult for use.

3)The solvent usage which causes the batch size to reduce and also the recovery problems.

The current invention uses Copper based catalyst with the modifying agent which improves the selectivity without the usage of the solvent and also avoids the formation of Dimethyl octanol (by product) instead it develops Hydrocarbons which are relatively low boiling and can be easily separated.

Terpenes are easily available from both natural and synthetic sources. They form the base for the synthesis of various agro based or drug API but the biggest challenge is the side reaction these terpenes easily undergo during chemical reactions. Controlling the conditions is very tricky and also separation of these byproducts/impurities become a much more difficult task.

But along with the disadvantages they have some added advantage that the byproducts, if separable, can also be used or sold.

The Hydrogenation has been widely studied in terpene chemistry over the years but the real skill lies in the development of method which satisfies the following two conditions

- Selective hydrogenation
- Cost effective hydrogenation.

Most of the reductions involving noble metals mentioned in the various papers are either not commercially viable because the cost of noble metal catalysts is really expensive or sometimes reusability is an issue.

The use of cheaper catalysts like nickel, cobalt etc. solves the problem of cost but on the other hand has a problem of selectivity and hence introduces the factor of separation which is again a tedious job.

Some of the catalysts like copper chromite etc have handling issues like being carcinogenic which is also one of the reasons that they are not preferred despite good selectivity and cost effectiveness.

The present invention deals with the usage of the copper as a catalyst which has been known for many years. Copper acts as both cost effective as well as with the help of suitable modifiers can be a good reducing agents. But the modifiers should be such that it reduces hydrogenolysis.

The copper can be used as a dust but is generally preferred with a certain base like Al2O3 etc.in a suitable percentages like depending upon the requirement of the reaction. The paper[29] show the use of the various copper catalyst in different proportions with as well as without solvents By optimizing the conditions the paper suggest the full conversion of the geraniol to Citronellol with the formation of no side products .But the use of the solvent reduces the batch size i.e. amount of Citronellol generated per day.

The material used for the current discussion consists of the use of the geraniol/Nerol in the pure form or as a mixture but the sum of isomers can be >90% Catalyst used CuO/Al_2O_3 from BASF (Cu-0226S).Other materials can also be used like citral etc but the conversion vary depending upon the conditions under which the hydrogenation is being carried out.

2. Results and Discussion: -

The general schematic representation of the geraniol/nerol to citronellol involves the following set of reaction

In the reduction of geraniol-nerol to citronellol involves the following four competitive reactions

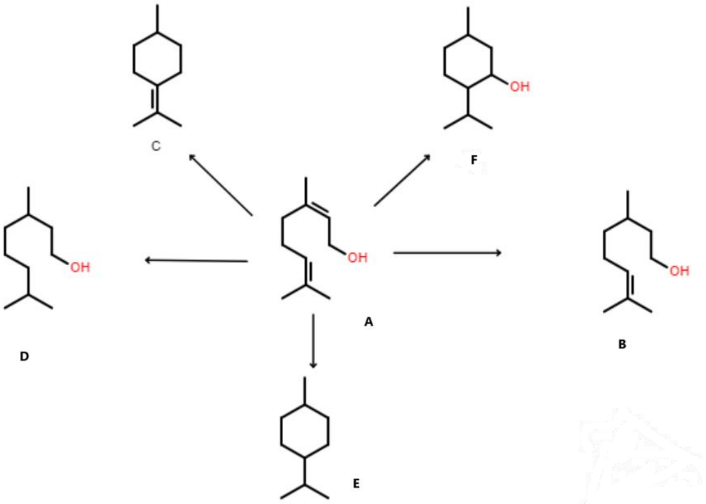
1) One reaction reduces the of the allylic double bonds

2) Another reaction involves the reduction of both allylic and non allylic double bonds

3) The cyclisation

4) Hydrogenolysis

Out of all possible reactions known the main purpose is to selectively reduce only one double bond by locking the allylic alcohol in one configuration and then addition of hydrogen to the double bond while the other double bond remains unaltered. Rather than reduction of the other double bond the reduction proceeds through the hydrogenolysis, this results in the formation of the hydrocarbons of different structures which can be easily separated via simple distillation.



Scheme 1 shows the possible products formed during the reactions

The reduction of the Geraniol to citronellol involves the various parameter changes i.e temperature, pressure, catalyst quantities etc .When substrate composition against conversion was studied it was found that the conversion was more or less the same. And the formation of B was also more or less the same which is indicative that the reduction is selective to the allylic double bonds. This shows that the allylic bond reduction is the predominant reaction and the next is hydrogenolysis, where the total reduction take place with the loss of water.

Table 1A shows the conversion Vs the substrate composition with the other parameters unchanged Substrate (various grades of Geraniol) Vs Conversion

Sr no	Substrate	Base	Catalyst	Pressure	Time	Temp	Catalyst: Substrate	Base: substrate	Conversion
1	Geraniol 70	NaOH (5% sol)	CuO/Al_2O_3	600 psi	2h	80-100C	2%	0.05%	70%

2	Geraniol 60	NaOH (5% sol)	CuO/Al_2O_3	600 psi	2h	80-100C	2%	0.05%	65%
3	Geraniol 98	NaOH (5% sol)	CuO/Al_2O_3	600 psi	2h	80-100C	2%	0.05%	68%
4	Geraniol 90	NaOH (5% sol)	CuO/Al_2O_3	600 psi	2h	80-100C	2%	0.05%	64%

Table 1B shows the GC selectivity.

Sr no	A (%)	B (%)	C (%)	D (%)	E (%)	F(%)	others
1	0.1	70	5	nil	18	0.5	6.4
2	0.2	68	4	nil	24	0.8	3
3	nil	72	3	nil	21	0.1	3.9
4	nil	65	5	nil	20	0.7	9.3

This is indicative that the substrate be geraniol pure or mixture of geraniol: nerol the reduction proceeds in the similar way.

Pressure has a remarkable effect on the rate and selectivity of the reduction reactions. However, in copper-based reduction reactions it is that high pressure is required, as copper catalysts do not operate well at lower pressure.

Table 2A shows the variation of Pressure against the conversion and selectivity.

Table 2A shows the Pressure(psi) Vs Conversion with the other parameters unchanged
Pressure Vs Conversion

Sr no	Substrate	Base	Catalyst	Pressure	Time	Temp	Catalyst: Substrate	Base: substrate	Conversion
1	Geraniol 70	NaOH (5% sol)	CuO/Al_2O_3	100 psi	2h	80-100C	2%	0.05%	30%
2	Geraniol 70	NaOH (5% sol)	CuO/Al_2O_3	200 psi	2h	80-100C	2%	0.05%	45%
3	Geraniol 70	NaOH (5% sol)	CuO/Al_2O_3	300 psi	2h	80-100C	2%	0.05%	65%
4	Geraniol 70	NaOH (5% sol)	CuO/Al_2O_3	500 psi	2h	80-100C	2%	0.05%	72%

Table 2B shows the GC selectivity for selectivity Vs pressure of reactions

Sr no	A(%)	B(%)	C(%)	D(%)	E(%)	F(%)	Others
1	20	30	45	nil	2	1	2
2	10	21	41	nil	8	3	17
3	5	55	27	nil	5	5	3
4	nil	70	21	nil	2	6	1

From the above table 2A and 2B it is very clear that with the increase in the pressure the reaction proceeds at a good rate and the amount of the side reaction is also very less .It has been found in various papers that the reduction without the modifiers is generally non selective and especially in the case of the copper based catalyst, base generally acts as a modifier which enhances the selectivity.Here in this case lots of bases have been tried but hydroxides of the alkali metals are mostly found to be most selective and with a quantity less than 0.5-8% with respect to the catalyst and 5% dilution with water. With more concentration of the catalyst poisons the catalyst completely.

Table 3A shows the effect of the bases against conversion Conversion table of Base/modifiers Vs conversion

Sr no	Substrate	Base	Catalyst	Pressure	Time	Temp	Catalyst: Substrate	Base: substrate	Conversion
1	Geraniol 70	NaOH (50% sol)	CuO/Al_2O_3	500 psi	2h	80-100C	2%	0.05%	20%
2	Geraniol 70	NaOH (5% sol)	CuO/Al_2O_3	500 psi	2h	80-100C	2%	0.05%	68%
3	Geraniol 70	TEA	CuO/Al_2O_3	500 psi	2h	80-100C	2%	0.05%	No reaction
4	Geraniol 70	Mg(OH)2	CuO/Al_2O_3	500 psi	2h	80-100C	2%	0.05%	10%

Table 4B: Selectivity table of bases/modifiers Vs selectivity

Sr no	A(%)	B(%)	C(%)	D(%)	E(%)	F(%)	Others
1	50	45	5	nil	nil	nil	nil
2	nil	71	15	nil	7	3	17
3	70	nil	nil	nil	nil	nil	nil
4	60	5	2	nil	nil	nil	3

From the table 3A and 3B its is very clear that the reaction proceeds with the diluted bases and its specific concentrations which is indicative that only a small quantity of modifiers(bases) are required for the reaction and of the various organic and inorganic modifiers the alkaline hydroxide are found to be the best.

3. Conclusion:

The catalyst along with the base serves as the best method for the conversion of the geraniol mixtures into citronellol with the formation of the hydrocarbons which can be easily removed by simple distillation.

The above process serves as one of the best methods as it removes the solvent usages as the solvent reduces the batch size which is very problematic on a commercial scale.

The main advantage that the process offers is that in the reaction there is no formation of dimethyl octanol(complete hydrogenated product) which is difficult to remove during distillation and introduces a fatty note to the citronellol thereby reducing both price and value.

Experimental Section:

GC with the nitrogen as a carrier gas, FID detector, DB-wax capillary column with 30mm ID is used.

For the confirmation of the product's standard samples from authentic manufacturers like BASF, DRT is used as a reference. Vacuum pumps are used ranging from 10-0.5 torr, along with long Distillation columns for effective Separations are used. For reactions the catalyst used was BASF (Cu-0226S), geraniol was of various grades readily available in the fragrance industries and bases from the Merck.

100 mg Geraniol 70 (the remaining 26 being a mixture of nerol, isonerol, iso geraniol) was added in autoclave. 2mg of the activated catalyst was charged along with 0.1mg (5% caustic solution).

The reaction was monitored at different time intervals and the H_2 pressure was set at 100-600 psi H_2 pressure and temp from 25-180^{O}C.The reaction was stopped after disappearance of the geraniol peak.

The product was confirmed by GC MS and NMR (300 MHz).

References

[1] M. Eggersdorfer, in: Ullmanns Encyclopaedia. of IndustrialChemistry. 5th edn., vol. A26, VCH, Weinheim, 1993, pp. 205 – 220; b) K. A. D. Swift, Topics in Catalysis 2004, 27, 143 – 155; c) J. L. F. Monteiro, C. O. Veloso, Topics in Catalysis 2004, 27, 169 – 180.

[2] N. Ravasio, F. Zaccheria, M. Guidotti, R. Psaro, Topics in Catalysis 2004, 27, 157 – 168.

[3] N. Ravasio, N. Poli, R. Psaro, M. Saba, F. Zaccheria,Topics in Catalysis 2000, 213, 195 – 199; b) N. Ravasio, V. Leo, F. Babudri, M. Gargano, Tetrahedron Lett. 1997, 38, 7103 – 7106.

[4] M. Guidotti, G. Moretti, R. Psaro, N. Ravasio, Chem.Commun. 2000, 1789 – 1790.

[5] aH. Takaya, T. Ohta, S. Noboru, H. Kumobayashi, S.Akutagawa, S. Inoue, I. Kasahara, R. Noyori, J. Am. Chem. Soc. 1987, 109, 1596 – 1597; b) Y. Sun, C. Le Blond, J. Wang, D. G. Blackmond, J. Laquidara, J. R. Sowa, J. Am. Chem. Soc. 1995, 117,12647 – 12648; c) T.Benincori, E. Cesarotti, O. Piccolo, F. Sannicolo` , J.Org. Chem. 2000, 65, 2043.

[6] R. Adams, B. S. Garvey, J. Am. Chem. Soc. 1926, 48, 477 – 482; b) V. Grignard, R. Escourrou, Bull. Soc. Chim. Fr. 1925, 37, 546 – 548.

[7] D. Tas, R. F. Parton, K. Vercruysse, P. A. Jacobs, Stud.Surf. Sci. Catal. 1997, 105B, 1261.

[8] H. Kuna, K. Takahashi, M. Shibagaki, H. Matsushita,Bull. Chem. Soc. Japan 1989, 62, 3779.

[9] Jpn Kokai Tokyo Koho, Japanese Patent 5,702,4320, 1982;Chem. Abstr. 1982, 96, 181460.

[10] V. Paul, Indian Patent IN 147167, 1979; Chem. Abstr.1979, 93, 95442.

[11] C. Milone, C. Gangemi, R. Ingoglia, G. Neri, S. Galvagno, Appl. Catal. A 2000, 184, 89.

[12] F. Iosif, S. Coman, V. Parvulescu, P. Grange, S. Del Sarte,D. De Vos, P. Jacobs, Chem. Commun. 2004, 1292.

[13] A. F. Trasarti, A. J. Marchi, C. R. ApesteguOa, J. Catal.2004, 224, 484 – 488.

[14] J. Shabtai, R. Lazar, E. Biron, J. Mol. Catal. 1984, 27,35 – 43.

[15] F. Zaccheria, N. Ravasio, A. Fusi, R. Psaro, Chem. Commun.2005, 253 – 255.

[16] R. Uma, C. Cre´ visy, R. Gre´ e, Chem. Rev. 2003, 103, 27–51.

[17] B. M. Trost, R. J. Kulawiec, J. Am. Chem. Soc. 1993, 115,2027 – 2036.

[18] I. E. Marko` , A. Gautier, M. Sukazaki, A. Llobet, E.Plantalech-Mir, C. J. Urch, S. M. Brown, Angew. Chem. Int. Ed. 1999, 38, 1960 – 1962.

[19] N. Ravasio, M. Antenori, F. Babudri, M. Gargano, Stud.Surf. Sci. Catal. 1997, 108, 625 – 632.

[20] N. Ravasio, R. Psaro, F. Zaccheria, in: Catalysis of Organic Reactions, (Ed.: D. Morrel), Chem. Ind. Series, Marcel Dekker, New York, 2003, pp. 263 – 271.

[21] H.-G. Goebbel, T. Gerlach, G. Wegner, H. Fuchs, S. Unverricht,A. Salden, (BASF AG), PCTInt. Appl. WO 2004007411 A1, 2004; Chem. Abstr. 2004, 140, 128533.
[22] N. Ravasio, R. Psaro, F. Zaccheria, Tetrahedron Lett. 2002, 43, 3943 – 3945.
[23] H. Bricout, E. Monflier, J.-F. Carpentier, A. Mortreux, Eur. J. Inorg. Chem. 1998, 1739 – 1744.
[24] H. van Bekkum, P. Gallezot (Eds.), Topics in Catalysis, Special Issue: Catalytic Conversion of Renewables, 2004, 27, 1–4.
[25] M. Marchetti, B. Sechi, M. Usai, Chim. Ind. 2004, 86,52 – 56; b) J. C. Yori, D. L. Manuale, A. J. Marchi, J. M. Grau, Appl. Catal. A 2004, 275, 221 – 226; c) P. Hazra, A. P. Kahol, S. Mondal, Research and Industry 1992, 37, 106 – 109.
[26] F. Funke, T. Gerlach, K. Ebel, S. Unverricht, F. Haese, K.Burkart, H.-G. Gobbel, (BASF AG), US Patent 0158453, 2003; Chem. Abstr. 2003, 139, 22361.
[27] N. Ravasio, F. Zaccheria, M. Gargano, S. Recchia, A. Fusi, N. Poli, R. Psaro, Appl. Catal. A, 2002, 233, 1–6.
[28] F. Boccuzzi, G. Martra, S. Coluccia, N. Ravasio, J. Catal.1999, 184, 316 – 326. FULL PAPERS F. Zaccheria et al.1272.
[29]F Zaccheria, F., Ravasio, N., Fusi, A., Rodondi, M., & Psaro, R. (2005). Tuning Selectivity in Terpene Chemistry: Selective Hydrogenationversus Cascade Reactions over Copper Catalysts. Advanced Synthesis & Catalysis, 347(9), 1267–1272.