The Catalytic Method of Verbanol Preparation with Controlled Isomer Distribution Starting from Renewable Material α-Pinene

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Abstract

The reasonable scheme of commercially valuable odour chemicals syntheses starting from renewable natural material α-pinene includes the explored reaction of verbenol hydrogenation into verbanol under mild conditions over Pd/C catalyst. The possibility of verbanol stereoisomers preparation with controlled isomer distribution that defines a practical use of scheme as a whole is considered. The effects of the hydrogen pressure, temperature and catalyst content on the isomers reproportioning in the course of verbanol hydrogenation are studied. The main factors permitting the hydrogenation process to direct to the definite verbanol isomers production were found to be hydrogen pressure and reaction temperature. Isoverbanol/neoisoverbanol ratio increases with hydrogen pressure growth from 2 to 11 bar and temperature decrease from 50 to 90 °C.

INTRODUCTION

Recently such popular renewable source as α-pinene attracts more and more attention of chemists searching different profitable methods of valuable wide-consumable compound production (medicines, fragrances and vitamins). α-Pinene is an inexpensive component of raw turpentine commercially available in large amounts. The perspective scheme of fragrance preparation starting from α-pinene is presented below (Scheme 1).

![Scheme 1](image)

Along with the rather described in the literature step of α-pinene air oxidation [1] it includes insufficiently known reaction of verbenol hydrogenation into saturated alcohol verbanol which is the starting material for the following syntheses of the new chemicals with unique properties. So verbanol can be converted in fragrance 3,4,6-trimethylhept-5-enal with strong lemon aroma. Hydrogenolysis of verbanol results in o-menthol that has a mild sweet odor somewhat suggestive of cloves and in this respect is unlike ordinary menthol. Because of
its pleasant odor, it is useful in scenting soaps, cosmetic bases and in other perfumery applications. When converted to its salicyclic ester it is useful as sun screening compound having optimum ultra violet filter properties, while other aromatic and aliphatic esters, preferably the higher ones, are useful as plasticizers, lubricants, cosmetics and the like [2].

Verbanol can be obtained by the molecular hydrogen reduction of verbenol in the presence of Ni, Pd, Pt catalysts. Note, that only a few of twelve theoretically possible forms of verbanol (eight optically active and four racemic) have been isolated in pure form. Thus, hydrogenation of cis- and trans-verbenol is known to result in following stereoisomers with eventual different reactivities [2-4] (Scheme 2).

According to [5] hydrogenation of cis-verbanol leads to cis-verbanol whereas hydrogenation of trans-verbenol gives trans-verbanol, but their structures were not assigned. The comparison of parameters of verbanol isomers patterns with ones of verbanol isomers obtained permit authors to conclude that cis-verbanol is neoisoverbanol and trans-verbanol is isoverbanol [3]. Authors [4] report that isomers content depends on catalyst employed. Thus, trans-verbanol hydrogenation over platinum oxide leads to isoverbanol (91 %) and verbanol (9 %) formations whereas hydrogenation of trans-verbenol over Pd/C gives isoverbanol (55 %) and verbanol (45 %). Catalytic hydrogenation of cis-verbenol yields neoisoverbanol [4].

It is important to note that because of the difference in reactivities these stereoisomers can give a lot of indistinguishable products in next step (including side by-products) that can distort strongly desirable odor of aim product. However the reasons causing the required isomer formation as well as kinetics of verbenol hydrogenation haven’t been yet considered in literature.

Earlier it has been found that the stereoselectivity of α-pinene hydrogenation over Pd/C into cis- and trans-pinane isomers is determined by hydrogen pressure and reaction temperature. Thus, cis-pinane content increased with hydrogen pressure growing and temperature decreasing [6].

The aim of this work is to study the possibility for the achievement of predictable verbanol isomer distribution in the course of verbenol hydrogenation over Pd/C as well as the general peculiarities of verbanol isomers synthesis by cis-/trans-verbenol hydrogenation in the same reaction conditions.

**Experimental**

The sample of cis-/trans-isomer mixture of verbenol was obtained by α-pinene air oxidation followed by vacuum distillation of α-pinene excess and borate ester rectification from verbenol [7].

Solution of verbenol (0.02 mol) in n-butanol (10 cm³) was hydrogenated over 4 % Pd

![Scheme 2](image-url)
on carbon support Sibunit (5–50 μm of carbon fraction) in stainless steel autoclave (150 ml) supplied with electromagnetic stirrer.

Reaction mixture was separated from the catalyst and products were analysed chromatographically using 7 m × 3 mm column, Silicic-SE 30/Chromaton N-AW.

The reaction products were identified by VG-7070 GC/MS using a 25 m × 0.2 m quartz capillary column (Silicone SE-30).

RESULTS AND DISCUSSION

Routes of verbano isomers formation

According to GLC analysis there are two products of verbano isomers hydrogenation over Pd/C in the course of reaction. The side products of the cycle opening are not observed. Quantity of hydrogen uptake is equal to 1 mol H₂ per 1 mol of verbano. It permits to convert the time dependence of hydrogen uptake into verbano concentration expressed in relative units as ratio between current total product concentration (C) and initial (C₀) concentration of verbano mixture. Two linear parts on the kinetic curves of verbano hydrogenation have been found (Fig. 1): sharper at the beginning and slower at the end. It indicates that reactivities of cis- and trans-verbenols presenting in the initial mixture differ substantially.

According to the GLC analysis (Fig. 2) neo-verbano formation occurs preferably at the

![Graph](image)

Fig. 2. Effect of verbano conversion on verbano isomers content. Reaction conditions: verbano (0.154 mol/l) in n-butanol (10 cm³), 0.4 g 4 % Pd/C, T = 40 °C, P₂H₂ = 11 bar.

initial verbano conversion range and iso-verbano starts to form at verbano conversion more than 30 % (see Fig. 2). It permits to suppose that in the beginning of verbano conversion (up to 40 %) the hydrogen uptake corresponds to cis-verbano hydrogenation to form neo-verbano:

![Chemical Structure](image)

At higher verbano conversion the rate of hydrogen uptake corresponds to the rate of trans-verbano into iso-verbano hydrogenation:

![Chemical Structure](image)

Some increase of neo-verbano content (at verbano conversion more than 30 %) may be caused by isomerization of trans-verbano into cis-verbano over catalyst surface:

![Chemical Structure](image)

The linear character of kinetic curve (see Fig. 1) indicates that verbano isomers hydrogenation rates have the order on corresponding isomer concentration close to zero. Verbano is seemed to adsorb strongly over the Pd
surface and the rate determining step may be the interaction of it with hydrogen adsorbed.

Cis-/trans-verbenols hydrogenation rate constants ratio were appreciated to be \( k_{\text{cis}}/k_{\text{trans}} = 2.7 \) at 40 °C. Note, verbenol is bicyclic alcohol and the side of the molecule bearing the two geminal \(-\text{CH}_3\) groups (β side), is severely hindered in comparison with the opposite side (α side). The trans-orientation of the \(-\text{OH}\) group in trans-verbenol makes the α side sterically nearly equal to the hindered β side. Taking into account that molecule approach to the catalyst surface generally occurs from the less hindered side, intermediate cis-verbenyl palladium π-complex is more stable than trans-verbenyl one and its formation proceeds more rapidly (Scheme 3).

Thus, the higher reactivity of cis-verbenol seems to be explained by favorable mutual cis-orientation of \(-\text{OH}\) and \(-\text{CH}_3\) functional groups in cis-verbenol molecule.

**Kinetic peculiarities**

**Effect of catalyst concentration.** Dependence of initial hydrogenation rate \( (W_o) \) upon catalyst concentration is linear in the range of explored temperatures and hydrogen pressures. It demonstrates the absence of hydrogen mass transfer limitation during experiments.

To elucidate the factors effected on the re-proportioning of verbenol isomers in the course of verbenol hydrogenation a set of experiments have been performed where temperature was varied from 30 to 90 °C and hydrogen pressure was varied from 2 to 11 bar.

**Effect of \( P_{\text{H}_2} \).** Dependence of initial hydrogenation rate \( (W_o) \) upon hydrogen pressure is of linear character. It indicates that hydrogenation rate has the first order on hydrogen pressure.

The hydrogen pressure increase favors the isoverbenol formation (Fig. 3, a). The decreasing of \( P_{\text{H}_2} \) causes the hydrogen adsorbed concentration diminution. The lack of hydrogen on the catalyst surface at low \( P_{\text{H}_2} \) seems to intensify the process of trans-verbenol isomerization into cis-verbenol.

**Effect of the temperature.** Verbenol hydrogenation rate increases with the temperature growth from 30 to 90 °C. Arrhenius plot of reaction rate temperature dependence has two linear parts. Activation energies of verbenol hydrogenation are 45.8 kJ/mol at the low temperature and 8.8 kJ/mol at higher one.

It was found that the ratio isoverbenol/neoverbenol doesn’t change in the range from 30 to 60 °C but declines quickly with temperature growth (see Fig. 3, b). Obviously the temperature rise leads to the decrease of hydrogen adsorbed concentration on the catalyst surface and to the cis-verbenol into trans-verbenol isomerization.
CONCLUSION

The general peculiarities of verbenol synthesis by verbenol hydrogenation over Pd/C in mild conditions have been studied. Macrokinetic data of verbenol isomers catalytic hydrogenation have been obtained. The routes of verbenol isomers formation including the isomerization step have been proposed. The main factors permitting to direct the hydrogenation process to the definite verbenol isomers production were found to be hydrogen pressure and reaction temperature. Isoverbenol/neoverbenol ratio increases with hydrogen pressure growth from 2 to 11 bar and temperature decrease from 50 to 90 °C in the course of hydrogenation over the catalyst Pd/C. The possibility of verbenol stereoisomers preparation with controlled isomer distribution conforms the advisability of industrial application of this scheme (involving explored reaction of verbenol preparation) for valuable odour chemical syntheses starting from renewable natural material α-pineene.

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REFERENCES

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