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

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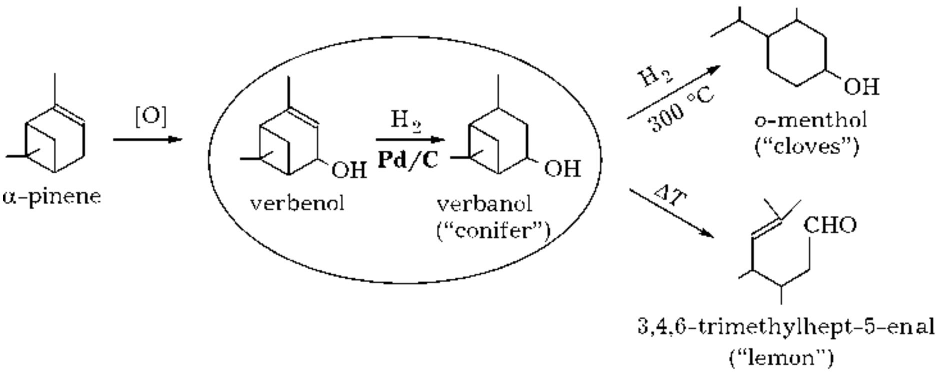
Abstract

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 verbenol 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).

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



Scheme 1.

its pleasant odor, it is useful in scenting soaps, cosmetic bases and in other perfumery applications. When converted to its salicylic 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 fore 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*-verbenol 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*-verbenol 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.

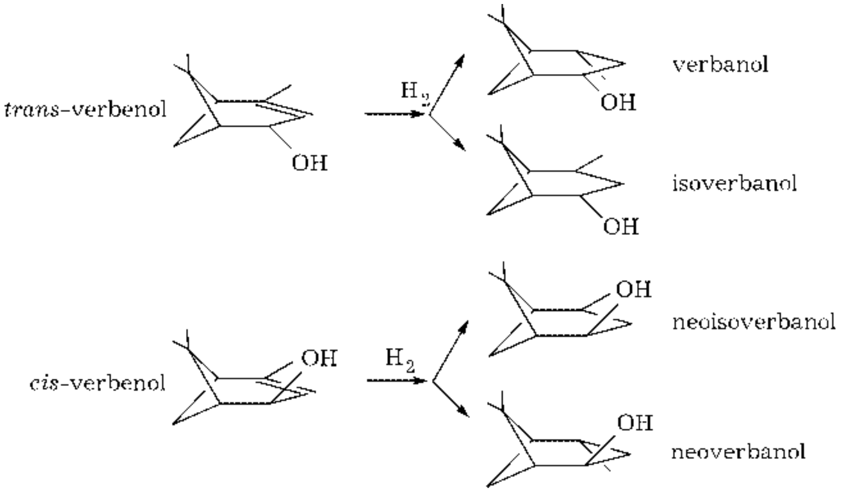
Earlier it has been found that the stereoselectivity of α-pinene hydrogenation over Pd/C into *cis*- and *trans*-pinane isomers is determined by hydrogen pressure and reaction temperature. Thus, *cis*-pinane content increased with hydrogen pressure growing and temperature decreasing [6].

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 verbenon [7].

Solution of verbenol (0.02 mol) in *n*-butanol (10 cm^3) was hydrogenated over 4 % Pd



Scheme 2.

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, Silicone 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 verbanol isomers formation

According to GLC analysis there are two products of verbenol 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 H_2 per 1 mol of verbenol. It permits to convert the time dependence of hydrogen uptake into verbenol concentration expressed in relative units as ratio between current total product concentration (C) and initial (C_0) concentration of verbenol mixture. Two linear parts on the kinetic curves of verbenol 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.

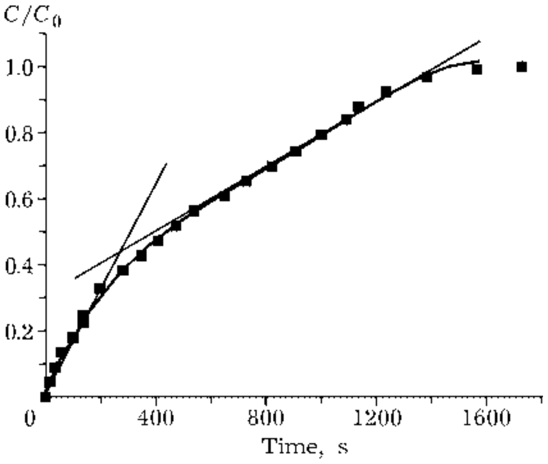


Fig. 1. Kinetic curve of product mixture formation. Reaction conditions: verbenol (0.154 mol/l) in *n*-butanol (10 cm^3), P_{H_2} = 11 bar, T = 50 °C, 0.2 g 4 % Pd/C.

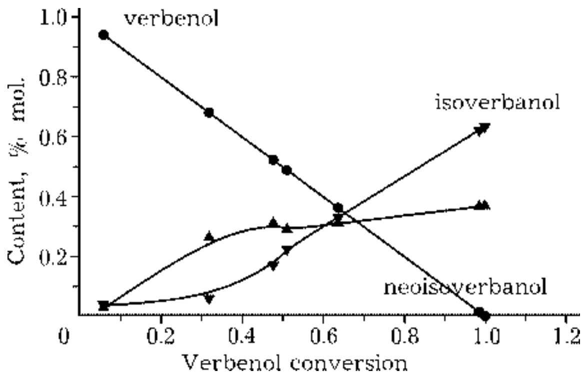
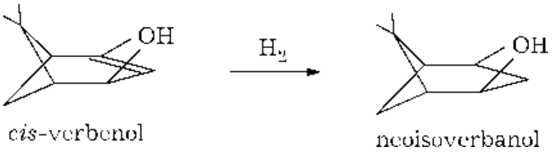
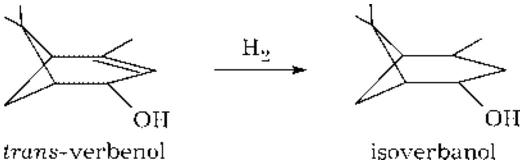


Fig. 2. Effect of verbenol conversion on verbanol isomers content. Reaction conditions: verbenol (0.154 mol/l) in *n*-butanol (10 cm^3), 0.4 g 4 % Pd/C, T = 40 °C, P_{H_2} = 11 bar.

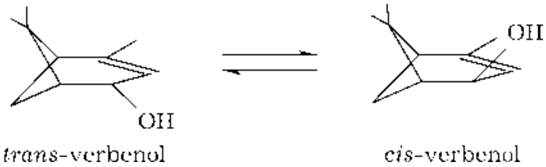
According to the GLC analysis (Fig. 2) neoisoverbanol formation occurs preferably at the initial verbenol conversion range and isoverbanol starts to form at verbenol conversion more than 30 % (see Fig. 2). It permits to suppose that in the beginning of verbenol conversion (up to 40 %) the hydrogen uptake corresponds to *cis*-verbenol hydrogenation to form neoisoverbanol:



At higher verbenol conversion the rate of hydrogen uptake corresponds to the rate of *trans*-verbenol into isoverbanol hydrogenation:



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



The linear character of kinetic curve (see Fig. 1) indicates that verbenol isomers hydrogenation rates have the order on corresponding isomer concentration close to zero. Verbenol 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 $k_{cis}/k_{trans} = 2.7$ at 40 °C. Note, verbenol is bicyclic alcohol and the side of the molecule bearing the two geminal $-CH_3$ groups (β side), is severely hindered in comparison with the opposite side (α side). The *trans*-orientation of the –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 –OH and $-CH_3$ functional groups in *cis*-verbenol molecule.

Kinetic peculiarities

Effect of catalyst concentration. Dependence of initial hydrogenation rate (W_0) 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 reproportioning of verbanol 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.

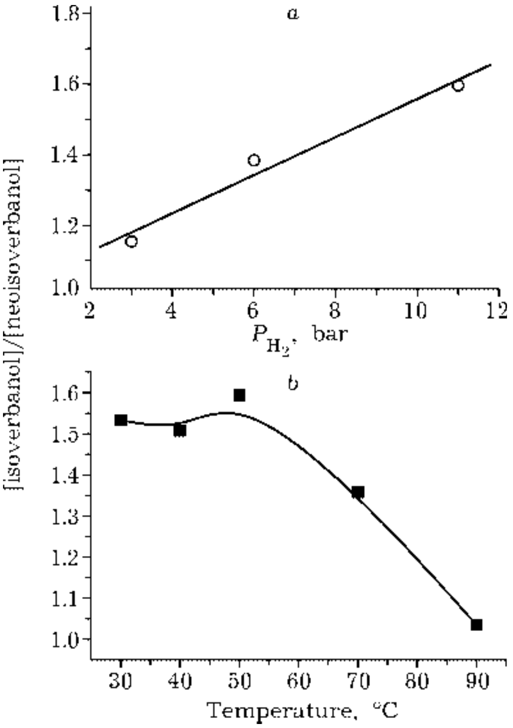
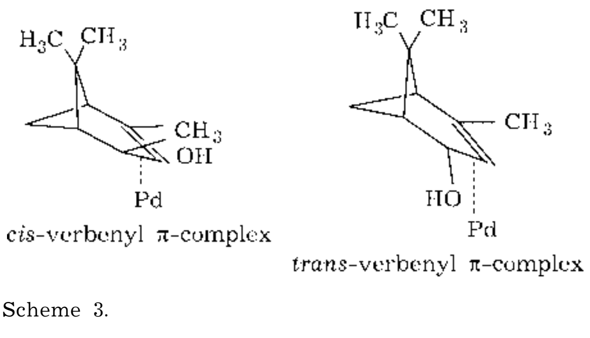


Fig. 3. Effect of P_{H_2} (*a*) and temperature (*b*) on the isoverbanol/neoisoverbanol ratio. Reaction conditions: verbenol (0.154 mol/l) in *n*-butanol (10 cm^3), 0.2 g 4 % Pd/C, T = 50 °C (*a*) P_{H_2} = 11 bar (*b*).

Effect of P_{H_2}. Dependence of initial hydrogenation rate (W_0) upon hydrogen pressure is of linear character. It indicates that hydrogenation rate has the first order on hydrogen pressure.



Scheme 3.

The hydrogen pressure increase favors the isoverbanol formation (Fig. 3, *a*). The decreasing of P_{H_2} causes the hydrogen adsorbed concentration diminution. The lack of hydrogen on the catalyst surface at low P_{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 isoverbanol/neoisoverbanol 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 verbanol 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 verbanol isomers formation including the isomerization step have been proposed. The main factors permitting to direct the hydrogenation process 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 in the course of hydrogenation over the catalyst Pd/C. The possibility of verbanol stereoisomers preparation with controlled isomer distribution conforms the advisability of industrial application of this scheme (involving explored reaction of verbanol preparation) for valuable odour chemical syntheses starting from renewable natural material α-pinene.

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