



# Selective one-pot carvone oxime hydrogenation over titania supported gold catalyst as a novel approach for dihydrocarvone synthesis



Yu. S. Demidova<sup>a,b</sup>, E.V. Suslov<sup>c</sup>, O.A. Simakova<sup>d</sup>, K.P. Volcho<sup>b,c</sup>, N.F. Salakhutdinov<sup>b,c</sup>, I.L. Simakova<sup>a,b,\*</sup>, D. Yu. Murzin<sup>d</sup>

<sup>a</sup> Borskov Institute of Catalysis, 630090, pr. Lavrentieva, 5, Novosibirsk, Russia

<sup>b</sup> Novosibirsk State University, 630090, Pirogova 2, Novosibirsk, Russia

<sup>c</sup> Novosibirsk Institute of Organic Chemistry, 630090, pr. Lavrentieva, 9, Novosibirsk, Russia

<sup>d</sup> Process Chemistry Centre, Åbo Akademi University, FI-20500, Turku/Åbo, Finland

## ARTICLE INFO

### Article history:

Received 10 November 2015

Received in revised form 14 April 2016

Accepted 15 April 2016

Available online 19 April 2016

### Keywords:

Gold catalyst

Chemoselective hydrogenation

Carvone oxime

Dihydrocarvone

Stereoselectivity

## ABSTRACT

It was shown for the first time that dihydrocarvone can be selectively produced by gold-catalyzed one-pot transformation of carvone oxime. This reaction was carried out at 100 °C under hydrogen pressure of 9 bar over 1.9 wt.% Au/TiO<sub>2</sub> catalyst using methanol as a solvent. Dihydrocarvone synthesis was shown to occur via carvone formation with the subsequent hydrogenation of its conjugated C=C double bond. Application of Au/TiO<sub>2</sub> catalyst for both deoxygenation and selective hydrogenation of olefinic C=C functional group is reported for the first time. The combination of these steps provides optimization of the synthetic method for dihydrocarvone production from carvone oxime which is a key intermediate in carvone synthesis from limonene. Despite a lower reaction rate than in the case of carvone, a significant increase in the stereoselectivity towards *trans*-dihydrocarvone was observed in the case of carvone oxime hydrogenation. The ratio between *trans*- and *cis*-dihydrocarvone was close to 4.0 compared to 1.8 achieved in the case of carvone hydrogenation.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

Dihydrocarvone is a valuable product that has a spearmint-like odor and is used as a flavoring additive in food industry. It is typically formed as a mixture of two stereoisomers and may be obtained starting from biomass derived carvone hydrogenation using molecular hydrogen over Ni, Pt, Pd, Rh, Ru catalysts [1–8]. This reaction path requires hydrogenation of conjugated C=C double bond in the presence of other unsaturated functional groups, such as C=O and an isolated C=C bonds. Application of the above mentioned catalysts typically favors hydrogenation of other unsaturated functional groups, resulting in formation of a complex mixture, with the target dihydrocarvone yield being less than 30%. In our previous work stereo- and chemoselective carvone hydrogenation to dihydrocarvone catalyzed by Au/TiO<sub>2</sub> catalyst with predominant formation of the *trans*-isomer was reported for the first time [9].

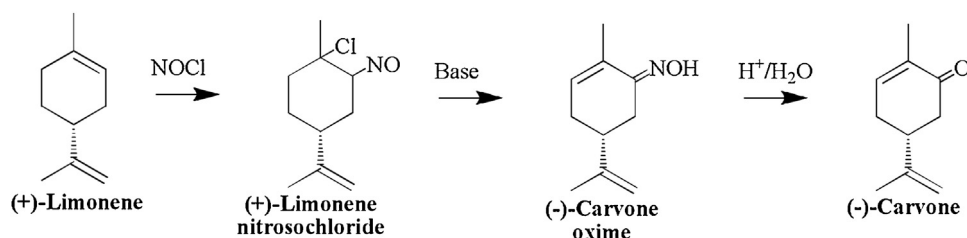
This novel approach is of significant interest in terms of a possibility to obtain industrially valuable dihydrocarvone via direct carvone hydrogenation. The highest total selectivity to dihydrocarvone (62%) was achieved at a nearly complete carvone conversion (90%) after 13 h, with the *trans*-to-*cis*-dihydrocarvone ratio being about 1.8.

Despite that (+)- and (–)-carvones can be isolated by fractional distillation of caraway and spearmint oils, respectively, currently carvones are mainly produced semi-synthetically starting from (+)- and (–)-limonenes through intermediate formation of carvone oxime (Scheme 1) [10,11]. Acid hydrolysis of the oxime group in the presence of a hydroxylamine acceptor, such as acetone, yields the target compound-carvone. From the viewpoint of improving the chemical synthesis efficiency, a one-pot multistep carvone oxime transformation to dihydrocarvone can be a promising approach.

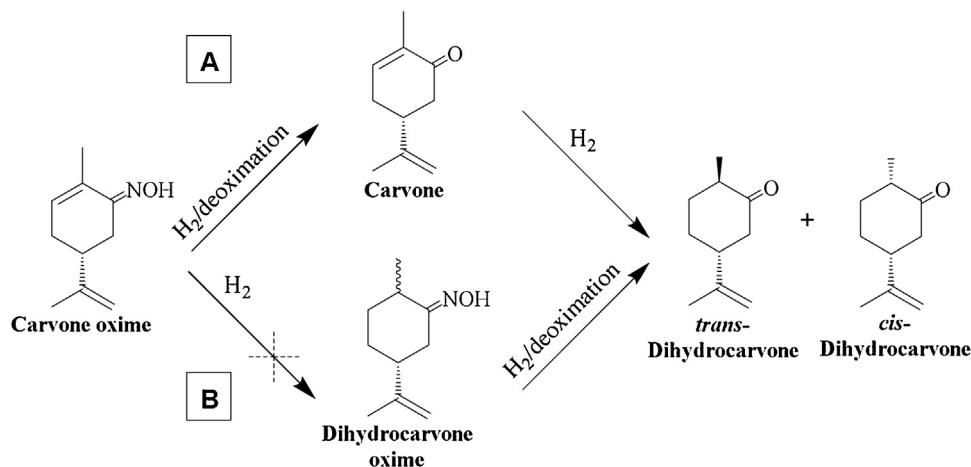
According to the literature data there are a few examples of direct carvone oxime conversion into dihydrocarvone including attempts of consecutive reduction via a corresponding ketone using LiAlH<sub>4</sub> in hexamethylphosphoramide (HMPA) [12] or by application of cell suspension cultures of *Nicotiana tabacum*, which promoted a slow formation of the target dihydrocarvone in a relatively low yield as a part of a complex mixture [13]. Despite a higher

\* Corresponding author at: Borskov Institute of Catalysis, 630090, pr. Lavrentieva, 5, Novosibirsk, Russia.

E-mail addresses: [simakova@catalysis.ru](mailto:simakova@catalysis.ru), [simakova-home@mail.ru](mailto:simakova-home@mail.ru) (I.L. Simakova).



Scheme 1. Industrial method of carvone synthesis [10,11].



Scheme 2. Possible reaction pathways for carvone formation from carvone oxime over Au/TiO<sub>2</sub>.

dihydrocarvone yield achieved by using the LiAlH<sub>4</sub>/HMPA system, the method has significant disadvantages in terms of practical and ecological considerations.

As it is well known, oximes possess a relatively high hydrolytic stability compared to imines [14]. According to the literature oximes can be also catalytically hydrogenated to produce imines or other nitrogen-containing derivatives followed by their further hydrolysis to form ketones [15–17]. Recently gold nanoparticles supported on TiO<sub>2</sub> or Fe<sub>2</sub>O<sub>3</sub> were shown by Corma and co-workers to be highly active in chemoselective hydrogenation of a nitro-group in the presence of other reducible functional groups [18–21]. Furthermore, highly catalytically active yolk-shell Au-CeO<sub>2</sub>@ZrO<sub>2</sub> nanoreactors were applied recently for the 4-nitrophenol selective reduction to 4-aminophenol [22]. More conventional platinum group metal catalysts along with the nitro-group hydrogenation can also activate olefinic or carbonyl groups due to stronger interactions with other functional groups [19,21,23–25]. Noteworthy is also, that application of more inexpensive metal as an active component, such as copper-containing catalysts, results in a preferable hydrogenation of a carbonyl group into hydroxyl group [26]. In this connection application of gold catalysts for oxime consecutive transformations to dihydrocarvone may be of high relevance.

As it was mentioned above an outstanding activity of Au/TiO<sub>2</sub> catalyst in carvone hydrogenation to valuable dihydrocarvone was previously demonstrated in our work. As a next step this study is focused on one-pot process consisting of sequential transformations of carvone oxime which is a key intermediate in carvone synthesis from limonene to dihydrocarvone. The combination of these steps can provide optimization of the synthetic method for dihydrocarvone production and moreover will exclude acid hydrolysis in an aqueous medium making dihydrocarvone synthesis more efficient in line with the guidelines of green chemistry. To the best of our knowledge there were no reports in the open literature on

heterogeneous catalysts for both deoxygenation and selective hydrogenation of olefinic C=C functional group.

Thus the goal of this work was to study regularities of carvone oxime transformation over Au/TiO<sub>2</sub> catalyst with the main aim to explore feasibility of the one-pot synthesis of dihydrocarvone starting from carvone oxime.

## 2. Experimental

### 2.1. Starting materials

(-)-Carvone (Aldrich, ≥97%), (5*R*)-dihydrocarvone (SAFC, ≥97%, mixture of *trans*- and *cis*-isomers 4:1) and methanol (J.T. Baker, ≥99.8%) were purchased from commercial suppliers and used as received. (-)-Carvone oxime and (2*R*,5*R*,*E*)-dihydrocarvone oxime were synthesized according to the methods presented below. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of the compounds were recorded by Bruker AV-400 spectrometer (400.13 MHz (<sup>1</sup>H), 100.61 MHz (<sup>13</sup>C)) in the CDCl<sub>3</sub> solutions.

### 2.2. Synthesis of (-)-carvone oxime and (2*R*,5*R*,*E*)-dihydrocarvone oxime

First to obtain (-)-carvone oxime a 100-ml round-bottom flask was charged with hydroxylamine hydrochloride (13.4 mmol, 0.93 g), sodium acetate (13.4 mmol, 1.10 g), (-)-carvone (6.67 mmol, 1.00 g, [α]<sub>D</sub><sup>20</sup> = -58 (*c* = neat)), methanol (20 ml) and water (17 ml). The solution was stirred for 4 days at r.t. and then water (100 ml) was added. The reaction mixture was extracted with ethyl acetate (EtOAc) (3 × 50 ml). The combined organic phase was washed with saturated sodium bicarbonate (2 × 25 ml), brine (2 × 25 ml) and then dried (Na<sub>2</sub>SO<sub>4</sub>). As a result, (-)-carvone oxime (0.83 g (75%)) was obtained. The synthesized (-)-carvone oxime was characterized by <sup>13</sup>C and <sup>1</sup>H NMR (supplementary data,

Download English Version:

<https://daneshyari.com/en/article/64587>

Download Persian Version:

<https://daneshyari.com/article/64587>

[Daneshyari.com](https://daneshyari.com)