Electronic supplementary materials *Mendeleev Commun.*, 2019, **29**, 380–381

Simple H_2-free hydrogenation of unsaturated monoterpenoids catalyzed by Raney nickel

Alexey A. Philippov, Andrey M. Chibiryaev and Oleg N. Martyanov

1. Solvents and reagents

All solvents and reagents were obtained from commercial sources and used as received: aluminum–nickel alloy (purum, 50% Al basis and 50% Ni basis, Sigma-Aldrich), NaOH (pellets, ≥99%, Akzo Nobel) propan-2-ol (≥99.5%, Sigma–Aldrich), hex-5-en-2-one (99%, Sigma-Aldrich), cyclohexanone (≥99%, Sigma-Aldrich), (*2S,5R*)-(–)-menthone (97%, *L*-menthone, Alfa Aesar), (*1R,4R*)-(+)-camphor (≥98%, TCI), citral (95%, Sigma-Aldrich), (*R*)-(–)-carvone (98%, Sigma-Aldrich) and sulfolane (99.0%, Aldrich).

2. Preparation of Raney nickel

Aluminum–nickel alloy (Raney alloy, 0.450 g) was added portionwise (portions of ~ 0.05 g) to 20% aq. NaOH (5.6 ml) for 15 min under vigorous stirring. The reaction was exothermic and intensive H_2 gas evolution was observed. The reaction temperature was maintained at 50–60°C. After all the alloy was added, the reaction mixture was kept under vigorous stirring for 45 min until the H_2 evolution ceased. After decantation of the aqueous alkali solution, the nickel precipitate was washed with distilled water (4 × 50 ml) until neutral pH. Further, the catalyst was washed with more water (15 ml) under vigorous stirring for 1.5 h at room temperature. For further washing and removing the water, the last one was then replaced by propan-2-ol (4 × 50 ml). The thus prepared nickel sample was pyrophoric enough and was usually used immediately after the preparation.

3. Experimental set-up

The scheme of autoclave reactor is shown in Figure S1. The reactor comprises a 285 ml high-temperature batch reactor of Autoclave Engineers (**A**). Hastelloy C-276 alloy is the wall material. The autoclave is equipped with the mechanical agitator MagneDrive® (Autoclave Engineers), two thermocouples (**T1, T2**), and sampling system (**S**) with a 6-port injector Valco C1-2006. The starting alcoholic solution of reactants is loaded from the vessel by using a high

pressure syringe pump Teledyne ISCO 260D (**C**). During the reaction, the mixer speed and the temperatures **T1** and **T2** are regulated by a programmable logic Sentinel controller (**B**), which additionally registers reaction pressure by electronic pressure sensor (**P**).

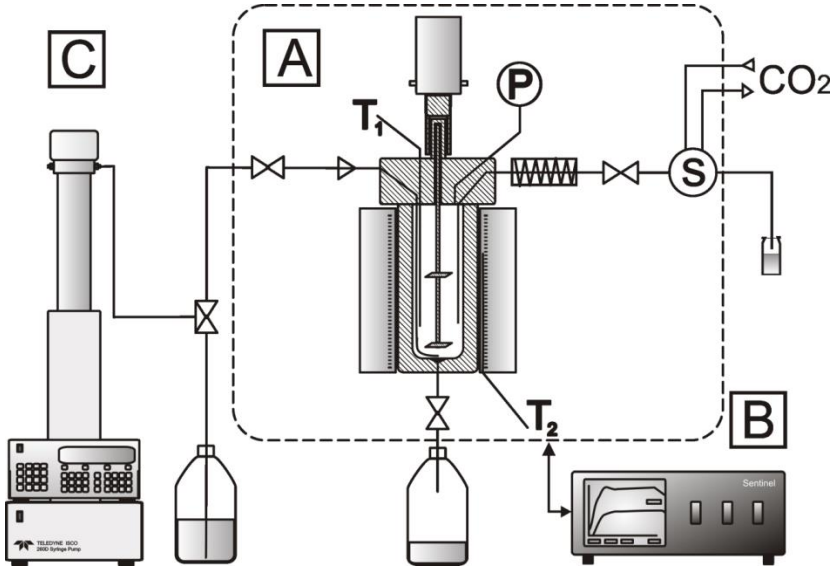

Figure S1. The experimental setup.

4. Catalyzed transfer hydrogenation

The initial reaction solution was prepared from three components: propan-2-ol (123–127 ml, 1.5 mol), substrate (0.30-0.50 g, 3.2 mmol), and sulfolane (0.25 g, 0.21 mmol, internal standard). This mixture was charged with freshly prepared Raney nickel (0.25 g, ~3.8 mmol). The reaction was performed in an autoclave or in s glass reactor for 5 h after the reactor reached 150°C (11 atm, $Pr^{i}OH$ self-pressure) and 82°C (1 atm), respectively. The reactor was blown with argon and then heated to the specified temperature for 10-15 min. The mixing rate was 800 rpm and 300 rpm for autoclave and glass reactors, respectively. The sampling was performed after 5 h at specified temperature.

5. Analysis of reaction mixtures

For qualitative and quantitative analysis of the reaction composition, a Shimadzu GCMS–QP2010 SE chromato-mass spectrometer equipped with an autosampler was used. Injection volume was 0.2 ml; all samples were diluted three times before analysis. A VF-5ms capillary chromatographic column (5% phenyl and 95% dimethylpolysiloxane) was chosen (length 30 m, internal diameter 0.25 mm, stationary phase thickness 0.25 μm). The temperature mode of column conditioning was: 50°C for 1 min, programmed heating up to 280°C at a rate of 15°C per minute, and subsequent conditioning in a stationary mode at 280°C for 2 min. The evaporator

temperature was 250°C, split 1:25, helium was as a carrier gas, constant flow rate of the carrier gas was 1.8 ml min^{-1}.

The products were identified using the peak retention time and the mass spectrum of the substance, which were compared with the corresponding data for pure compounds or with the data from the NIST and Wiley7 electronic mass spectral libraries.

The conversion of the substrates and the product yield were evaluated by the internal standard method with sulfolane as a standard.

Representative chromatograms of the final reaction mixtures

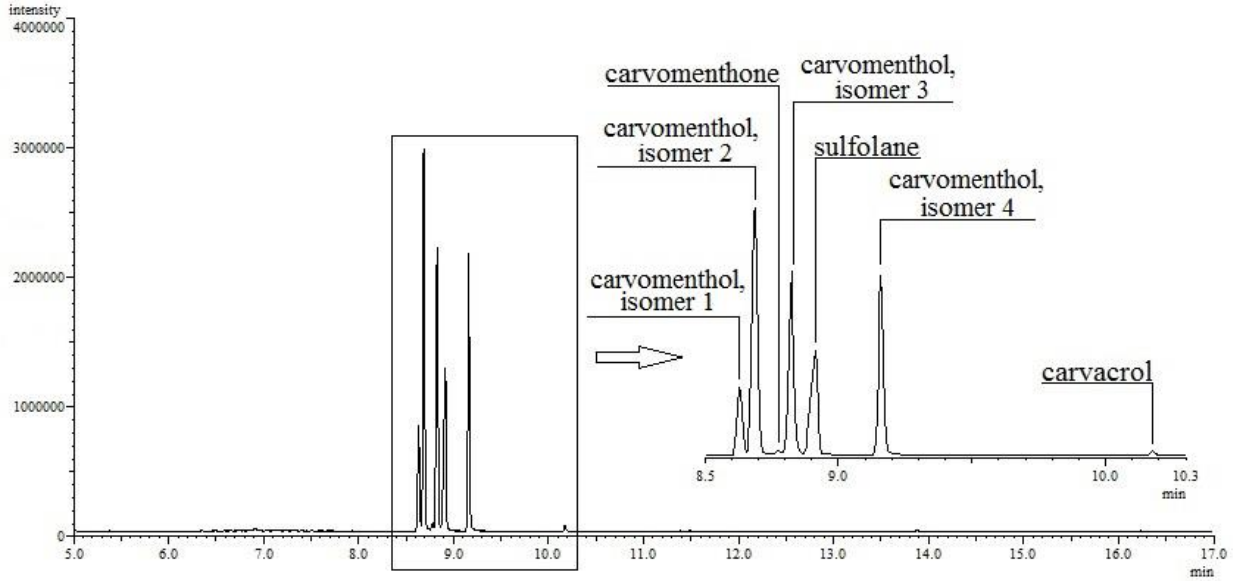

Figure S2. The final reaction mixture of carvone conversion at 150°C.

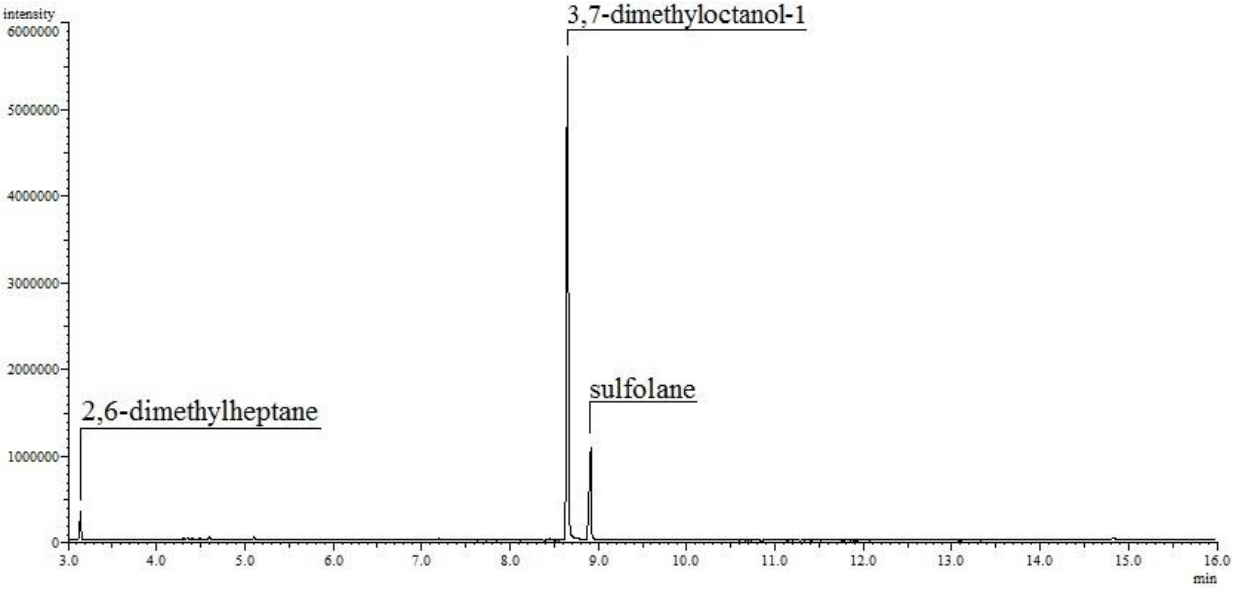

Figure S3. The final reaction mixture of citral conversion at 150°C.