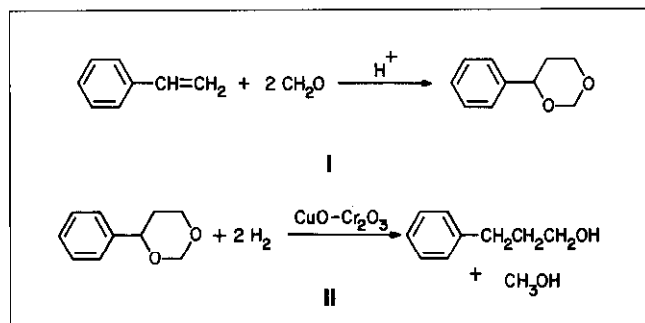


# 3-Cyclohexylpropanal and 3-Cyclohexylbutanal as Raw Materials for Fragrant Compounds

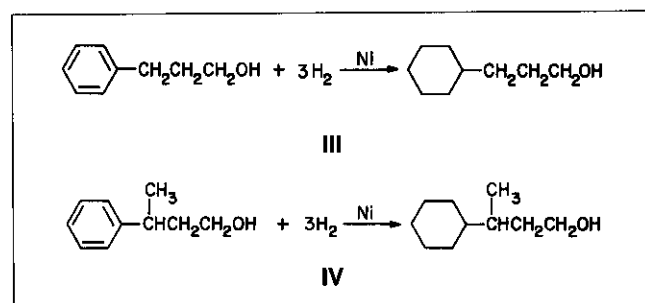
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3-Phenyl-1-propanol and 3-phenyl-1-butanol can be obtained with relative ease<sup>1</sup> by a two-step synthesis from styrene or  $\alpha$ -methylstyrene. In the first step a Prins' reaction with formaldehyde affords the respective substituted 1,3-dioxane (Reaction I) which, in the second step, undergoes hydrogenolysis to yield a phenyl substituted alcohol (Reaction II).



Similarly, 3-phenyl-1-butanol may be obtained from  $\alpha$ -methylstyrene via 4-methyl-4-phenyl-1,3-dioxane. Both phenyl substituted alcohols are important fragrant compounds themselves, similar to a number of their derivatives.<sup>2</sup>

This study reports an investigation of the hydrogenation of aromatic rings of these alcohols, leading to the respective

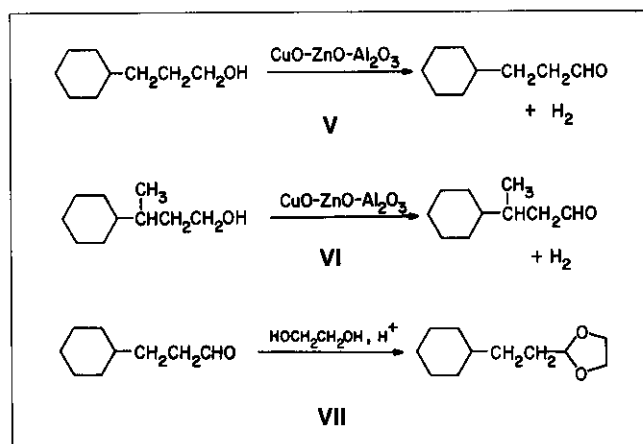


3-cyclohexyl-1-alkanols (Reactions III and IV).

The latter may also be regarded as fragrant compounds and as starting raw materials for the synthesis of compounds of other odor types. The dehydrogenation of both alcohols to aldehydes (Reactions V and VI) was investigated. These compounds are also odoriferous and are suitable raw materials for the preparation of fragrant acetals. In this work, acetals of both aldehydes with ethylene glycol and 1,2-propylene glycol were prepared and described (Reaction VII). Preparation of other acetals proceeded in a similar way.

## Experimental

**Chemicals:** 3-Phenyl-1-propanol and 3-phenyl-1-butanol were commercial products (Astrid Zidovice), purified by rectification. The hydrogenation catalyst was Ni/Al<sub>2</sub>O<sub>3</sub> (No. 6524 Leuna Werke, Germany); the dehydrogenation catalyst was CuO-ZnO-Al<sub>2</sub>O<sub>3</sub> (No. 1962 Leuna Werke, Germany). Ethylene glycol (Lachema, Brno), 1,2-propylene glycol (Astrid, Prague) and p-toluene sulfonic acid, as catalyst, were used to prepare the acetals.



**Apparatus:** The hydrogenations were carried out in a 400 ml autoclave and stirred with a two-propeller stirrer with a magnetic gear provided with a manometer, a thermocouple detector and a heating jacket. For 150 mL of 3-phenyl-1-propanol or 3-phenyl-1-butanol, 3.5 g of catalyst was used, the reaction temperature was 179-188°C, the pressure varied in the range 6.5-10 MPa.

An apparatus reported earlier<sup>3</sup> was used in the dehydrogenations. The reactor consisted of a glass tube, inner diameter 7 mm, 410 mm long. A tube, inner diameter 3 mm, was sealed to the lower narrow part of the reactor, a flock of glass wadding was placed in the broader part of the reactor, with a layer of the catalyst situated above. After evaporation and preheating of the injected alcohol, a glass tube (6.1 x 300 mm) with a wound stainless wire, 0.2 mm in diameter was inserted into the space above the catalyst. A small tube intended for the insertion of the thermocouple into the catalyst bed was attached to the end of the glass tube. The reactor was situated in a tube furnace consisting of a system of three concentric glass tubes, of which the two outer ones served as heat insulators, while the inner tube, 12 mm in diameter, had a resistance wire wound around the whole length of it and served as a heating tube. The temperature was regulated by means of a TRS-193 regulator, combined

with an electronic BA-04 regulator, and was measured by using a Fe-Ko thermocouple with an accuracy  $\pm 2^\circ\text{C}$ .

3-Cyclohexyl-1-propanol and 3-cyclohexyl-1-butanol were added by means of a proportional piston pump PPM-Mikrotechne, Prague. Hydrogen and nitrogen were added through a flow regulator made at UACHP - Satalice, type 56; the flow rate was measured by a calibrated capillary flow meter. After leaving the reactor, the reaction mixture passed through a cooler and freezer and was analyzed by the gas chromatographic method.

The catalyst was reduced by a procedure described previously,<sup>3</sup> prior to use. Two g of catalyst, grain size 0.75-1.25, was used. Prior to measurement, the reactor was washed with hydrogen (25 mL/min) for 60 minutes at 250°C, after which the flow rate of hydrogen was reduced to 225 mL/h and the required temperature was adjusted by means of a regulator. On reaching the stationary state, addition of 3-cyclohexyl-1-propanol or 3-cyclohexyl-1-butanol was started. The stationary composition mixture was usually reached after 60 minutes; sampling took place at 15-30 minute intervals.

The acetals were prepared by reacting 0.5 mol of the respective aldehyde and 1 mol of glycol in the presence of 50 mL of toluene and 0.1g of p-toulene sulfonic acid. The mixture was heated to reflux, and water formed in the processes was continuously removed by means of an azeotropic head. On completion of the separation of water, the mixture was cooled and washed with a 5% solution of  $\text{NaHCO}_3$  and water. Toulene and the residual water were removed by distillation and the raw acetal was distilled in vacuo.

**Analytical Methods:** The analyses were performed with a Chrom 5 gas chromatograph provided with flame-ionization detection. A glass tube, 2.5m x 2.5mm, was used, packed with a 5% OV-25 on Chromaton NAW-HMDS, grain size 0.16-0.20 mm. The analyses were done at 130°C.

### Results and Discussion

**Catalytic hydrogenation of 3-phenyl-1-alkanols:** Conditions reported in the "Experimental" were found to be optimal for the series of experiments performed. The reaction time was 350 minutes, until the starting 3-phenyl-1-alkanol had disappeared. After that, the reaction mixture contained 6 wt.% of light foreruns and 94 wt.% of 3-cyclohexyl-1-alkanol. The reactivity of 3-phenyl-1-propanol and 3-phenyl-1-butanol was virtually the same.

Attempts to carry out hydrogenolysis of the respective phenyl substituted 1,3-dioxanes with simultaneous hydrogenation of the aromatic ring to 3-cyclohexyl-alkanols were not successful. During the hydrogenolysis and simultaneous hydrogenation of 4-phenyl-1,3-dioxane, a small amount of the methyl ester of 3-cyclohexylpropionic acid was also formed in the reaction mixture, but it could not be separated from 3-cyclohexyl-1-propanol by rectification, impairing the fragrance of the final product. In addition, the reaction was very slow. The hydrogenolysis and hydrogenation of 4-

Table I. Physico-chemical constants of the compounds

Compounds	b.p. (°C/kPa)	$n_D^{20}$	$\rho_4^{20}$
3-cyclohexyl-1-propanol	108-109/1.87	1.4671	0.9143
3-cyclohexylpropanal	79/1.87	1.4579	0.9463
2-(2-cyclohexylethyl)-1,3-dioxolane	115/1.87	1.4656	0.9723
2-(2-cyclohexylethyl)-4-methyl-1,3-dioxolane	112/1.87	1.4594	0.9225
3-cyclohexyl-1-butanol	111/1.87	1.4730	0.9217
2-cyclohexylbutanal	98.5-99/1.87	1.4632	0.9167
2-(2-cyclohexylpropyl)-1,3-dioxolane	123.5/1.73	1.4631	0.9687
2-(2-cyclohexylpropyl)-4-methyl-1,3-dioxolane	86/0.8	1.4649	0.9504

methyl-4-phenyl-1,3-dioxane did not lead to its total disappearance from the reaction mixture; also, its separation by distillation is questionable. Moreover, in this case distillation does not ensure good separation of 3-cyclohexyl-1-butanol from the intermediate, 3-phenyl-1-butanol.

*Catalytic dehydrogenation of 3-cyclohexyl-1-alkanols:* Under conditions described in the "Experimental" and found to be optimal (250°C, addition rate 0.64g of 3-cyclohexyl-1-propanol/min per 2g of catalyst), the reaction mixture in the stationary state contained 0.3 wt.% of degradation for foreruns, 58 wt.% of 3-cyclohexylpropanol, 0.7 wt.% of an unidentified compound and 41 wt.% of unreacted 3-cyclohexyl-1-propanol. The results of dehydrogenation of 3-cyclohexyl-1-butanol were similar.

*Preparation of acetals with ethylene glycol and 1,2-propylene glycol:* The acetals were prepared by employing a procedure reported in the experiment. The yields varied in the range 75-90% theoretical.

### Properties of the Compounds

The physico-chemical constants of the compounds are shown in Table I. Of these compounds, only the odor properties of 3-cyclohexyl-1-propanol have been reported in the literature where it has been described as possessing a very mild, sweet balsamic, but rather "flat" odor of moderate to poor tenacity.<sup>4</sup> It is less floral compared to hydrocinnamic alcohol, and does not have rosy character of that material.

3-Cyclohexyl-1-butanol has a woody, santal type, floral scent.<sup>5</sup> Both aldehydes, 3-cyclohexylpropanal and 3-cyclohexylbutanal, are floral green; 3-cyclohexylbutanal is waxy.

The fragrance characteristics of the acetals are as follows:

- 2-(2-cyclohexylethyl)-1,3-dioxolane: resembles tropical fruit (kiwi, mango)
- 2-(2-cyclohexyl)-4-methyl-1,3-dioxolane: finely spicy,

resembles peach

- 2-(2-cyclohexylpropyl)-1,3-dioxolane: scent of young leaves, fine resinous scent, resembles buds
- 2-(2-cyclohexylpropyl)-4-methyl-1,3-dioxolane: floral and fruity, resembles apricot and peach.

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