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Proceeding Paper

$CuBr_2/HY_{mmm}$—An Effective Catalyst for the Transformation of 1,2-propanediol into 2-ethyl-4-methyl-1,3-dioxolane †

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Abstract: Propanal is an important chemical intermediate used extensively in the manufacture of rubbers, plastics, paints, and pesticides. The ready availability of 1,2-propanediol production from glycerol provides the opportunity for propanal and its derivatives production from biomass resource. We found that pyrolysis of 1,2-propanediol at 200 °C for 4 h in the presence of the supported form of copper (II) bromide on micro-meso-macroporous zeolite HY_{mmm} (5 wt% $CuBr_2$(20%)/HY_{mmm}) gives a mixture of *cis*- and *trans*-2-ethyl-4-methyl-1,3-dioxolane in 1.5:1 ratio. New synthetic methodology paves the way to the development of new Cu-based catalytic systems promising for industrial applications.

Keywords: 1,2-propanediol; propanal derivatives; 2-ethyl-4-methyl-1,3-dioxolane; Cu-based immobilized catalyst

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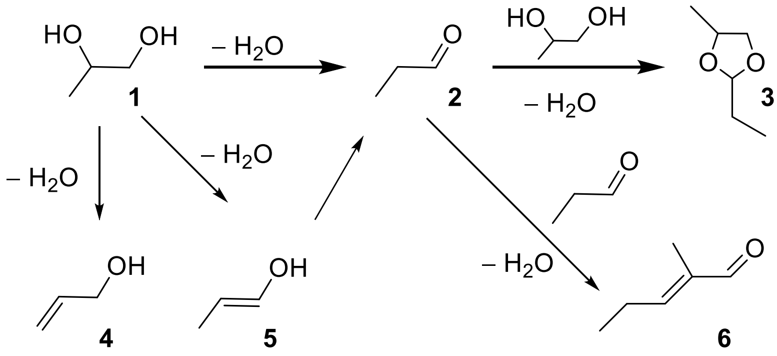
1. Introduction

It is known that 1,2-propanediol **1** can be transformed into propionaldehyde **2** in the presence of acid catalysts [1], heteropolyacids $H_4[SiMo_{12}O_{40}]$, $H_3[PMo_{12}O_{40}]$, $H_4[SiW_{12}O_{40}]$ and $H_3[PW_{12}O_{40}]$ [2,3], zeolite catalysts Theta-1 and ZSM-23 [4].

Such a strong acid as phosphotungstic acid ($H_3PW_{12}O_{40}$) is active in the dehydration of 1,2-propanediol **1** to propionaldehyde **2** accompanied by the formation of the corresponding dioxolanes **3** [2].

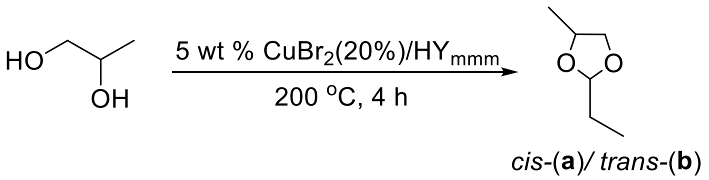
Mori K. et al. reported 100% conversion upon dehydration of 1,2-propanediol **1** on phosphotungstic acid on silica ($H_3PW_{12}O_{40}/SiO_2$) [3], but propanal **2** yield was relatively low due to side reaction of forming propanal **2** with 1,2-propanediol to give the cyclic acetal (2-ethyl-4-methyl-1,3-dioxolane) **3**.



Scheme 1. Possible products of 1,2-propanediol **1** dehydration and propanal **2** condensation.

2. Results and Discussion

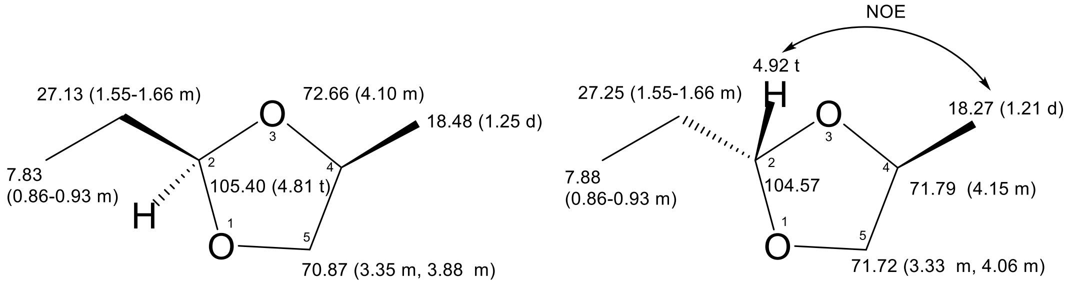
We synthesized $CuBr_2$ supported micro-meso-macroporous zeolite HY_{mmm} (5 wt% $CuBr_2$(20%)/HY_{mmm}). The use of 5 wt% $CuBr_2$(20%)/HY_{mmm} as a catalyst allowed us to selectively synthesize dioxolanes **3**. We assume that the reaction proceeds through the stage of propanal **2** formation. Then the propanal **2** reacts with the 1,2-propanediol **1** to form cyclic acetals **3**. Under conditions of 200 °C for 4 h, we obtained *cis*-2-ethyl-4-methyl-1,3-dioxolane **3a** and *trans*-2-ethyl-4-methyl-1,3-dioxolane **3b** in almost 100% yields (1.5:1).



1 **3**

Scheme 2. Selective synthesis of dioxolanes **3** from 1,2-propanediol **1**.

To establish the configuration of substituents in isomers **3a** and **3b**, we used the results of NOESY experiment, in which a cross-peak of the methyl group signal was found for the minor (*trans*) isomer **3b** at δ(C-4) = 1.21 ppm with a proton signal δ(H-C-2) = 4.92 ppm (Figure 1).



3a **a : b = 1.5 : 1** **3b**

Figure 1. The spectral parameters of *cis*-2-ethyl-4-methyl-1,3-dioxolane **3a** and *trans*-2-ethyl-4-methyl-1,3-dioxolane **3b**.

3. Conclusions

Thus, the $CuBr_2$ supported zeolite HY_{mmm} with a hierarchical porous structure showed high activity in the synthesis of *cis*-**3a** and *trans*-2-ethyl-4-methyl-1,3-dioxolanes **3b** from 1,2-propanediol **1**.

4. Experimental Part

Commercially available reagents were used. The reactions were carried out in a dry argon atmosphere. ^1H and ^{13}C NMR spectra were recorded on Bruker Avance 400 spectrometer (100.62 MHz for ^{13}C and 400.13 MHz for ^1H). When recording the ^1H and ^{13}C NMR spectra, $SiMe_4$ and $CDCl_3$ were used as an internal standards, respectively. Mass spectra were measured using Finnigan 4021 instrument with an ionizing electron energy of 70 eV and an ionization chamber temperature of 200 °C. The elemental analysis of the samples was determined on Carlo Erba elemental analyzer, model 1106.

Preparation of starting heterogeneous catalysts.

A heterogeneous catalyst - granular zeolite Y in the H-form (HY_{mmm}) with a high degree of crystallinity and a hierarchical micro-meso-macroporous structure was synthesized according to the procedure [5]. An immobilized $CuBr_2/HY_{mmm}$ catalyst with a copper (II) bromide content of 20 wt% was prepared by impregnating a HY_{mmm} zeolite with $CuBr_2$ solution in ethanol. $CuBr_2$ concentration was monitored by the water absorption of the HY_{mmm} zeolite. Subsequent drying and calcination of the catalyst was carried out at 170 °C.

The synthesis of 2-ethyl-4-methyl-1,3-dioxolane.

The reactions were carried out in a glass ampoule (V = 10 mL) placed in a stainless steel microautoclave (V = 17 mL) with constant stirring and controlled heating. An ampoule in an argon flow was charged with 5 wt% $CuBr_2/HY_{mmm}$ catalyst (10 mg), 2.6 mmol (200 mg) of 1,2-propanediol **1**. The sealed ampoule was placed in an autoclave, the autoclave was hermetically sealed and heated at 200 °C for 4 h. After the completion of the reaction, the autoclave was cooled to room temperature, the ampoule was opened, the reaction mixture was filtered through a paper filter (eluent - CH_2Cl_2). Methylene chloride was distilled off and the resulting clear solutions was dried with sodium sulfate, filtered and subjected to fractional distillation to give a mixture of *cis*-**3a** and *trans*-2-ethyl-4-methyl-dioxolane **3b** with a boiling point range of 110–115 °C. Compound identity was established by GC–MS, ^1H and ^{13}C NMR spectra.

Cis-2-ethyl-4-methyl-1,3-dioxolane (3a) and trans-2-ethyl-4-methyl-1,3-dioxolane (3b)

Yield 152 mg (100%), colorless liquid, Bp 110–115 °C. **3a**/**3b** ratio = 1.5:1. NMR ^{13}C, δ, ppm, **3a**: 7.83, 18.48, 27.13, 70.87, 72.66, 105.40; **3b**: 7.88, 18.27, 27.25, 71.72, 71.79, 104.57. NMR ^1H, δ, ppm, **3a**: 0.86 0.93 m (3H, $C\underline{H}_3CH_2$), 1.25 d (3H, CH_3, *J* 8.9 Hz), 1.55 1.66 m (2H, $CH_3C\underline{H}_2$), 3.35 m, 3.88 m (2H, C^5H_2), 4.10 m (1H, C^4H), 4.81 t (1H, C^2H, *J* 4.45 Hz); **3b**: 0.86–0.93 m (3H, $C\underline{H}_3CH_2$), 1.21 d (3H, CH_3, *J* 6.2 Hz), 1.55 1.66 m (2H, $CH_3C\underline{H}_2$), 3.33 m, 4.06 m (2H, C^5H_2), 4.15 m (1H, C^4H), 4.92 t (1H, C^2H, *J* 4.6 Hz).

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