# Production of Renewable 1,3-Pentadiene from Xylitol via Formic

## Acid-Mediated Deoxydehydration and Palladium-Catalyzed

## **Deoxygenation Reactions†**

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#### **Experimental**

**Materilas:** All chemicals were used as received. Xylitol (98%), formic acid (99%), tetraglyme (99%), ε-caprolactone (99%), 1,3-dimethylpropyleneurea (99%), cyclopentene (99%) and isooctanol (analytical reagent) were purchased from J&K Chemical. 5% Pd/C (150 meshes) was purchased from Sigma-Aldrich. 1,3-pentadiene (trans, >95%) was purchased from TCI. Raney Ni was purchased from Anshan Zhongli catalyst factory.

**Catalyst preparation:** 5% Pt/C and 5% Ru/C were prepared based on the incipient wetness impregnation method using an aqueous solution of  $H_2PtCl_6$  and  $RuCl_3$  as a precursor and active carbon (40-60 meshes) as a support, followed with drying at room temperature overnight and a period of heating at 120 °C for 8 h. The catalysts were reduced in a stream of  $H_2$  at 250 °C for 2 h. Prior to exposure to air, the catalyst was passivated under a stream of 1%  $O_2$  in  $N_2$  for 4 h.

**Xylitol deoxydehydration (DODH) to 2,4-pentadien-1-ol, 1-formate (2E) by formic acid (batch):** Typically, 12.0 g of xylitol and 43.6 g of formic acid were added into a 50 mL three-neck flask. The flask was heated by an electric apparatus with magnetic stirring and the thermal couple was immersed in the solution to control the temperature. After the reaction temperature reached 235 °C, the DODH reaction occurred accompanied by the distillation of the deoxygenated products. The products were collected by condensation using cooling water. The total reaction time including the feeding time was 12 h.

Xylitol deoxydehydration (DODH) to 2,4-pentadien-1-ol, 1-formate (2E) by formic acid (continuous): The DODH of xylitol was carried out in a continuous reaction system. Typically, 5 g of tetraglyme was added into a 50 mL three-neck flask and then heated to 235  $^{\circ}$ C by an electric apparatus with magnetic stirring. The thermal couple was immersed in tetraglyme to control the temperature. 12.0 g of xylitol was

dissolved in 43.6 g of formic acid to prepare a xylitol solution. After the reaction temperature reached 235  $^{\circ}$ C, the xylitol solution was fed into the flask at a rate of 4.4 mL/h by a constant-flow pump. The products were collected by condensation using cooling water. The overall reaction time was 12 h which included the feeding time.

The deoxygenation of 2,4-pentadien-1-ol, 1-formate (2E) to 1,3-pentadiene: The deoxygenation of 2,4-pentadien-1-ol, 1-formate (2E) was performed in a 25 mL high-pressure autoclave with a teflon liner. Typically, the autoclave was loaded with 0.1 g catalyst, 0.03 g cyclopentene (internal standard for the determination of 1,3-pentadiene), 0.04 g isooctanol (internal standard for the determination of conversion) and 6 g 0.33wt% 2,4-pentadien-1-ol, 1-formate (2E) ethanol solution before being sealed. The reactor was pressurized with N<sub>2</sub> to 1.3 MPa, then heated to 80 °C and kept at 80 °C for 3 h with magnetic stirring at 800 rpm. Once the reaction stopped, the reactor was cooled down with ice water bath. The gas and liquid products were collected for the GC analysis.

**Product analysis:** The products in the DODH reaction of xylitol were analysed by an Agilent 7890B GC equipped with a HP-INNWAX capillary column (30 m, 0.25 mm ID, 0.5 μm film) and a FID detector. Typically, after the reaction a certain amount of solution containing products were taken out form the flask, mixed with a designed amount of isooctanol (internal standard) and finally diluted by ethanol for analysis. The product of the deoxygenation of 2,4-pentadien-1-ol, 1-formate (2E) was analysed by an Agilent 7890B GC equipped with a HP-PLOT Q capillary column (30 m, 0.53 mm ID) and a FID detector. After the reaction, the solution containing products of the deoxygenation of 2,4-pentadien. The gas products of the deoxygenation of 2,4-pentadien. The solution containing products and internal standards were taken out for analysis without dilution. The gas products of the deoxygenation of 2,4-pentadien-1-ol, 1-formate (2E) were analysed by an Agilent 6890N GC equipped with a TDX-1 column and a TCD detector. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on Bruker AVANCE III 400 MHz.

**Batch distillation:** A packed distillation column (diameter: 15 mm, height: 1 m) filled with triangle auger fillers (2.5 cm height equivalent of theoretical plate) was used in this experiment. The bottom temperature (electric heating) was set as 130  $^{\circ}$ C and the insulation temperature of column was fixed at 140  $^{\circ}$ C. The overhead products were collected at the reflux ratio of 20:1.



**Fig. S1.** The <sup>1</sup>H NMR and <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>) spectra of 2,4-pentadien-1-ol, 1-formate (2E). After the reaction, the organic phase was extracted from the crude mixture by adding excessive amount of NaHCO<sub>3</sub>. The organic phase was further purified by silica gel column chromatography (ether/pentane 8/100) to separate 2,4-pentadien-1-ol, 1-formate (2E) from other chemicals. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ 8.08 (s, 1H), 6.44-6.26 (m, 2H), 5.84-5.72 (m, 1H), 5.28 (d, *J*= 15.7 Hz, 1H), 5.18 (d, *J*=

9.1 Hz, 1H), 4.70 (d, J = 6.4 Hz, 2H). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ 160.79, 135.86, 135.47, 126.37, 119.20, 64.08. Based on the fact that the configuration of 2,4-pentadien-1-ol was E (determined by <sup>1</sup>H NMR in the following) and 2,4-pentadien-1-ol, 1-formate (2E) was produced from the esterification of 2,4-pentadien-1-ol with formic acid, we concluded that the configuration of 2,4-pentadien-1-ol, 1-formate was also E.



**Fig. S2.** The <sup>1</sup>H NMR and <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>) spectra of the 2,4-pentadien-1-ol (2E).<sup>1</sup> The organic phase was extracted from the crude mixture by adding excessive amount of NaHCO<sub>3</sub>. The organic phase was further purified by silica gel column chromatography (ether/pentane 4/100) to separate 2,4-pentadien-1-ol (2E) from other chemicals. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ 6.46-6.19 (m, 2H), 5.85 (dt, *J* = 14.8, 5.8 Hz, 1H), 5.23 (d, *J* = 16.2 Hz, 1H), 5.11 (d, *J* = 9.6 Hz, 1H), 4.20 (d, J = 5.8 Hz, 2H). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  136.35, 132.50, 132.07, 117.81, 63.31. Based on the coupling constants, the configuration of 2,4-pentadien-1-ol was E.



**Fig. S3.** Photograph of the residue (dark brown oily viscous liquid) in the flask after reaction. (a) The residue of table 1 entry 1, (b) The residue of table 1 entry 2.



**Fig. S4.** Experimental device for the continuous reaction of formic acid-mediated DODH of xylitol to 2,4-pentadien-1-ol, 1-formate (2E).



**Fig. S5.** Photograph of the residue (yellowish-brown oily viscous liquid) of table 1 entry 3 in the flask after reaction.





**Fig. S6.** The <sup>1</sup>H NMR and <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>) spectra of 1,3-pentadiene obtained in this work. The purification of 1,3-pentadiene was conducted by the simple distillation. The crude products obtained from the deoxygenation of 2,4-pentadien-1-ol, 1-formate (2E) was directly used for the simple distillation. The distillation device is the same as the experimental device shown in Fig. S4 without feeding system. The temperature is controlled at 45 °C. 1,3-pentadiene was collected by ice water condensation. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  6.32 (dt, J = 17.0, 10.3 Hz, 1H), 6.18 – 5.97 (m, 1H), 5.73 (dq, J = 13.6, 6.7 Hz, 1H), 5.08 (d, J = 16.9 Hz, 1H), 4.95 (d, J = 10.1 Hz, 1H), 1.77 (d, J = 6.8 Hz, 3H). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  137.34, 132.44, 130.03, 114.51, 18.11. Based on the coupling constants, the configuration of 1,3-pentadiene was E.



**Fig. S7.** GC chromatogram of the gas products from the deoxygenation of 2,4-pentadien-1-ol, 1-formate (2E) to 1,3-pentadiene over 5% Pd/C at 80  $^{\circ}$ C for 3 h.

#### References

1. A. B. Smith, M. A. Foley, S. Dong and A. Orbin, J. Org. Chem., 2009, 74, 5987-6001.