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Synthesis of δ-Valerolactone

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Dehydrogenations of aliphatic glycols to the corresponding lactones with copper catalyst have been studied by several investigators. With copper chromite, Schiepp and Hachihama prepared δ-valerolactone by the dehydrogenation of 1,5-pentanediol which was obtained by the hydrogenation of δ-hydroxyvalerolactone. However, no study on catalytic dehydrogenation of hydroxyaldehyde which is supposed to be an intermediate in the lactone formation, is found in the literature. The results obtained in a previous study of the dehydrogenation of 1,4-butanediol to γ-butyrolactone with copper-zinc oxide, suggested that δ-valerolactone might be prepared from δ-hydroxyvalerolactone or 1,5-pentanediol with the same catalyst.

An attempt to dehydrogenate δ-hydroxyvalerolactone or 1,5-pentanediol with copper-zinc oxide in vapor phase has been successfully carried out to give δ-valerolactone in good yields. This procedure has an advantage over the air oxidation of 6-hydroxyvalerolactone with cobalt acetate.

The infrared spectrum of the product obtained from 8-hydroxyvalerolactone was the same with that of δ-valerolactone from 1,5-pentanediol (Fig. 1). It shows strong bands due to lactone group at 5.75, 8.63, and 9.46 μ, as described in the literature.

δ-Hydroxyvalerolactone was prepared by the hydrolysis of dihydropyran. Its infrared spectrum shows a strong band due to hydroxyl group at 2.96 μ and a weak band due to carbonyl group at 5.80 μ (Fig. 2). It is in accord with the fact that δ-hydroxyvalerolactone exists predominantly as the cyclic lactone, 2-hydroxyterahydropyran.

EXPERIMENTAL

3, 4-Dihydro-α-pyran. It was prepared by a catalytic conversion of tetrahydrofurfuryl alcohol over the activated alumina. From 102 g. of tetrahydrofurfuryl alcohol there was obtained 60 g. (71%) of dihydropyran, b. p. 85–86°C, nD20 1.4350, d425 0.9072 (lit. b. p. 84–86°C). MR: Found, 24.2; Calcd., 24.3.

δ-Hydroxyvalerolactone. From 60 g. of dihydropyran there was obtained 25 g. (33%) of 8-hydroxyvalerolactone, b. p. 64–65°C/3 mm Hg, nD20 1.4514, d425 1.0527 (lit. b. p. 54–55°C/3 mm Hg, nD20 1.4514, d425 1.0537). MR: Found, 26.2; Calcd. for the cyclic form, 26.3.


δ-Hydroxyvalerolactone gave a 2, 4-dinitrophenylhydrazone melting at 106–107°C (lit.10 109°C).

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NOTE

Wavelength, $\mu$.

Fig. 1. Infrared spectrum of 3-valerolactone.

Wavelength, $\mu$.

Fig. 2. Infrared spectrum of 3-hydroxyvaleroaldehyde.

Anal. Found: C, 46.99; H, 5.11. Calcd. for C$_7$H$_{14}$O$_2$N$_4$: C, 46.81; H, 5.00%.

Catalyst. The catalyst consisting of 20% copper and 80% zinc oxide which had been prepared previously for the dehydrogenation of 1,4-butanediol, was used. It was made in tablets, 8 mm in diameter and 2 mm in thickness.

Dehydrogenation of 1,5-pentanediol. The apparatus and the procedure for the dehydrogenation were essentially the same as those described previously.

The dehydrogenation tube (60 cm x 15 mm) packed with 50 ml. of the catalyst was heated in a furnace. Activation of the catalyst was carried out at 220°C in a stream of hydrogen until the reduction was completed. A quantity of 20 g. of 1,5-pentanediol (b.p. 115°C/3 mmHg, $n_0^{25}$ 1.4481, $d_4^{25}$ 0.9876) was introduced with 20 liters/hour of hydrogen in a period of two-hours. The reaction temperature was maintained at 230°C. The product was collected in a trap cooled with ice water, and distilled to yield 16.5 g. (86%) of 3-valerolactone, b.p. 73-75°C/3 mmHg, $n_0^{25}$ 1.4550, $d_4^{25}$ 1.1017 (lit. $n_0^{25}$ 1.4553, $d_4^{25}$ 1.104). MRD: Found, 24.7; Calcd. 24.7.

Anal. Found: C, 59.90; H, 8.16. Calcd. for C$_7$H$_{14}$O$_2$: C, 59.98; H, 8.05%.

Hydrazide of 3-valerolactone. 3-Valerolactone (0.5 g) was added into 0.5 ml. of 85% aqueous hydrazine hydrate. The mixture became clear with a evolution of heat and solidified on cooling. After a recrystallization from 95% ethanol, the hydrazide was obtained in colorless crystals melting at 105-106°C (lit.). It was very soluble in water.

Anal. Found: C, 45.62; H, 9.20. Calcd. for C$_7$H$_{14}$O$_2$N$_4$: C, 45.44; H, 9.15%.

Dehydrogenation of 3-hydroxyvaleroaldehyde. After the activation of the catalyst with hydrogen at 220°C for 2 hours, the pressure in the reaction system
NOTE

was reduced to 20~30 mmHg. δ-Hydroxyvaleraldehyde was introduced by vacuum distillation in a period of one-hour. The reaction temperature was maintained at 230°C. The sample (10g) gave 7.5g. (76%) of the product, b. p. 73~74°C/3mmHg, nD^20 1.4550, which was identified as δ-valerolactone. It formed a hydrazide, m. p. 105~106°C, which gave no depression when mixed with an authentic sample.

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