Title	Synthesis of δ-Valerolactone
Author(s)	Oka, Shinzaburo
Citation	Bulletin of the Institute for Chemical Research, Kyoto University (1961), 39(4-5): 322-324
Issue Date	1961-11-15
URL	http://hdl.handle.net/2433/75849
Right	
Type	Departmental Bulletin Paper
Textversion	publisher

Synthesis of δ-Valerolactone

Shinzaburo OKA*

(Kunichika Laboratory)

Received July 14, 1961

Dehydrogenations of aliphatic glycols to the corresponding lactones with copper catalyst have been studied by several investigators[1~6]. With copper chromite, Schiepp[3], and Hachihama[4] prepared δ-valerolactone by the dehydrogenation of 1, 5-pentanediol which was obtained by the hydrogenation of δ-hydroxyvaleroaldehyde. 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[7] of the dehydrogenationof 1, 4-butanediol to γ-butyrolactone with copper-zinc oxide, suggested that δ-valerolactone might be prepared from δ-hydroxyvaleroaldehyde or 1, 5-pentanediol with the same catalyst.

An attempt to dehydrogenate δ-hydroxyvaleroaldehyde 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 oxydation[4,8] of δ-hydroxyvaleroaldehyde to δ-valerolactone with cobalt acetate.

The infrared spectrum of the product obtained from δ-hydroxyvaleroaldehyde was the same with that of δ-valerolactone from 1, 5-pentanediol (Fig. 1). It shows strong bands due to lactone group at 5.75μ, 8.63μ and 9.46μ, as described in the literature[9].

δ-Hydroxyvaleroaldehyde was prepared by the hydrolysis of dihydropyran[10]. Its infrared spectrum shows a strong dand due to hydroxyl group at 2.96μ and a weak band due to carbonyl group at 5.80μ (Fig. 2). It is inaccord with the fact that δ-hydroxyvaleroaldehyde exists predominantly as the cyclic lactole, 2-hydroxyterahydropyran[11].

EXPERIMENTAL

3, 4-Dihydro-α-pyran. It was prepared by a catalytic conversion of tetrahydrofurfuryl alcohol over the activated alumina[12]. From 102 g. of tetrahydrofurfuryl alcohol there was obtained 60 g. (71%) of dihydropyran, b. p. 85~86°C, n_D^{25} 1.4350, d_4^{25} 0.9072 (lit.[12] b. p. 84~86°C). MR_D: Found, 24.2; Calcd., 24.3.

δ-Hydroxyvaleroaldehyde. From 60g. of dihydropyran there was obtained 25g. (33%) of δ-hydroxyvaleroaldehyde, b. p. 54~55°C/3mmHg, n_D^{25} 1.4515, d_4^{25} 1.0527 (lit.[13] b. p. 54~55°C/3mmHg, n_D^{25} 1.4514, d_4^{25} 1.0537). MR_D: Found, 26.2; Calcd. for the cyclic form, 26.3.

Anal. Found: C, 58.63; H, 9.95. Calcd. for $C_5H_{10}O_2$: C, 58.80; H, 9.87%.

δ-Hydroxyvaleroaldehyde gave a 2, 4-dinitrophenylhydrazone melting at 106~107°C (lit.[14] 109°C).

* 岡 信三郎

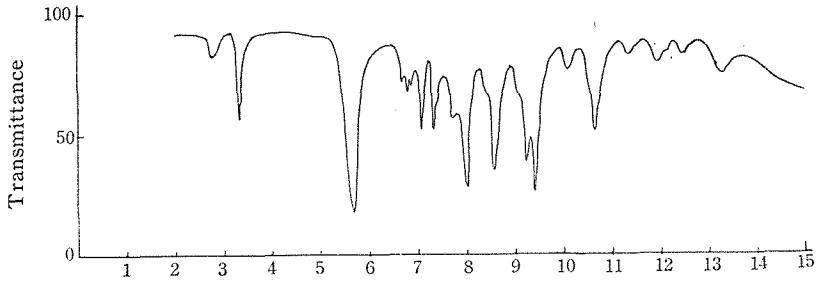

Fig. 1. Infrared spectrum of δ-valerolactone.

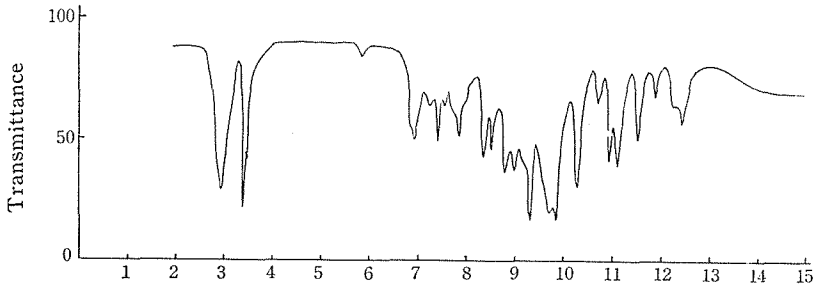

Fig. 2. Infrared spectrum of δ- hydroxyvaleroaldehyde.

Anal. Found: C, 46.99; H, 5.11. Calcd. for $C_{11}H_{14}O_5N_4$: 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[7], was used. It was made in tablets, 8 mm in diameter and 2mm in thickness.

Dehydrogenation of 1, 5-pentanediol. The apparatus and the procedure for the dehydrogenation were essentially the same as those described previously[7].

The dehydrogenation tube (60 cm × 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 guantity of 20g. of 1, 5-pentanediol (b. p. 115°C/3mmHg, n_D^{25} 1.4481, d_4^{25} 0.9876) was introduced with 20 l./hr. 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 16.5g. (86%) of δ-valerolactone, b. p. 73~75°C/3mmHg, n_D^{25} 1.4550, d_4^{25} 1.1017 (lit[8]. n_D^{25} 1.4553, d_4^{25} 1.104). MR_D: Found, 24.7; Calcd. 24.7.

Anal. Found: C, 59.90; H, 8.16. Calcd. for $C_5H_8O_2$: C, 59.98; H, 8.05%.

Hydrazide of δ-valerolactone. δ-Valerolactone (0.5g) was added into 0.5ml. 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[16]. 105~106°C). It was very soluble in water.

Anal. Found: C, 45.62; H, 9.20. Calcd. for $C_5H_{12}O_2N_2$: C, 45.44; H, 9.15%.

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

was reduced to 20~30 mmHg. δ-Hydroxyvaleroaldehyde 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, n_D^{25} 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.

ACKNOWLEDGMENT

The author wishes to express his sincere thanks to Prof. Sango Kunichika for invaluable advices and discussions. He also thanks Mr. T. Takenaka for the infrared spectra analyses and Mrs. T. Ikegami for the elementary analyses.

REFERENCES

(1) W. Reppe *et al.*, Ger. Pat. 699945 (1940) ; *Chem. Abstr.*, **35**, 6977 (1941).
(2) L. P. Kyrides *et al.*, *J. Am. Chem. Soc.*, **68**, 1385 (1946).
(3) L. E. Schniepp *et al.*, *ibid.*, **69**, 1545 (1947).
(4) Y. Hachihama *et al.*, *Chem. High Polymers* (Japan), **8**, 75 (1951).
(5) R. I. Longley *et al.*, *J. Am. Chem. Soc.* **74**, 2012 (1952).
(6) W. Reppe *et al.*, *Ann.*, **596**, 158 (1955).
(7) S. Oka, *Bull. Chem. Soc. Japan*, **34**, 12 (1961).
(8) J. G. M. Bremmer *et al.*, U. S. Pat. 2429799 (1947) ; *Chem. Abstr.*, **42**, 923 (1948).
(9) L. Birkofer, *Ber.*, **87**, 1192 (1954).
(10) G. F. Woods, "Organic Syntheses" **23**, 25 (1943).
(11) C. D. Hurd *et al.*, *J. Am. Chem. Soc.*, **74**, 5324 (1952).
(12) R. L. Sawyar *et al.*, "Organic Syntheses" **23**, 25 (1943).
(13) L. E. Schniepp *et al.*, *J. Am. Chem. Soc.*, **68**, 1646 (1946).
(14) G. F. Woods *et al.*, *ibid.*, **68**, 2111 (1946).
(15) R. Robinson *et al.*, *J. Chem. Soc.*, **1937**, 373.