

*The Synthesis of 3- α -Carboxyethylcyclopentanol Lactone**

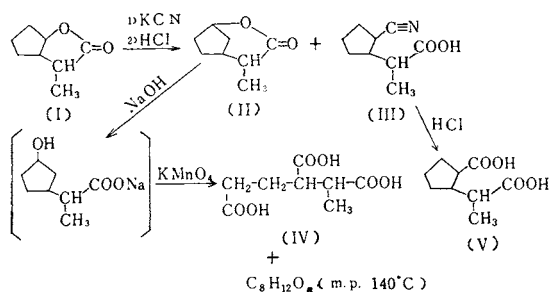
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The synthesis of *cis*- and *trans*-lactones of 2- α -carboxyethylcyclopentanol was previously reported¹⁾.

Now, *cis*-3- α -carboxyethylcyclopentanol lactone was obtained as one of the reaction products of *cis*-2- α -carboxyethylcyclopentanol lactone with potassium cyanide. The formation of this lactone indicates a possibility of a new rearrangement²⁾ reaction.

cis-2- α -Carboxyethylcyclopentanol lactone (I) was heated with potassium cyanide³⁾ in a sealed tube at 250~260°C for 24 hr., and the products were isolated and fractionally distilled. These were lactone $C_8H_{12}O_2$ (II) [b. p. 85~86°C/3.5 mmHg; $\lambda_{\text{EtOH}}^{\text{max}}$ 211 m μ , ν_{max} 5.83 μ ⁴⁾ (C=O), 8.24 μ (C-O); Found: C, 68.05; H, 8.80. Calcd. for $C_8H_{12}O_2$: C, 68.54; H, 8.63%] and a cyanoacid $C_9H_{13}O_2N$ (III) [b. p. 126~127°C/0.6 mmHg; $\lambda_{\text{EtOH}}^{\text{max}}$ 212.5 m μ , ν_{max} 5.84 μ (C=O), 4.42 μ (C \equiv N); Found: C, 64.12; H, 8.22; N, 6.99. Calcd. for $C_9H_{13}O_2N$: C, 64.65; H, 7.84; N, 8.38%].



The lactone (II) was hydrolyzed with 10% aqueous sodium hydroxide solution and the sodium salt solution of hydroxyacid was oxidized with potassium permanganate.

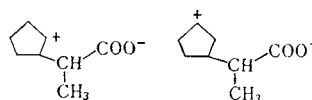
Tricarboxylic acids $C_8H_{12}O_6$ (IV) (m. p. 180°C; Found: C, 47.05; H, 6.28. Calcd. for $C_8H_{12}O_6$: C, 47.06; H, 5.92%), which was

identified as α -methyl- β -carboxyadipic acid⁵⁾ both by mixed melting point and infrared spectra, and $C_8H_{12}O_6$ (m. p. 140°C; Found: C, 47.26; H, 6.21. Calcd. for $C_8H_{12}O_6$: C, 47.06; H, 5.92%), which was not identified⁶⁾, were obtained as the oxidation products.

The formation of α -methyl- β -carboxyadipic acid suggested the structure (II) of *cis*-3- α -carboxyethylcyclopentanol lactone.

Hydrolysis of cyanoacid (III) with hydrochloric acid yielded a dicarboxylic acid $C_9H_{14}O_4$ (V) (m. p. 130°C; Found: C, 57.77; H, 7.62. Calcd. for $C_9H_{14}O_4$: C, 58.05; H, 7.58%) in agreement with the structure III of cyanoacid.

The conversion from *cis*-2- α -carboxyethylcyclopentanol lactone into *cis*-3- α -carboxyethylcyclopentanol lactone, would involve intermediates such as anion of III, and carbonium ions VI and VII.



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5) W. N. Haworth and W. H. Perkin, *J. Chem. Soc.*, 93, 581 (1908).

6) This acid showed melting point depression by mixed melting with authentic β -(α -carboxyethyl)-glutaric acid reported by Z. H. Skraup, *Monatsh.*, 21, 907 (1900).

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1) T. Tanaka, *This Bulletin*, 32, 1320 (1959).

2) C. C. Price and W. Kaplan, *J. Am. Chem. Soc.*, 66, 477 (1944).

3) G. Komppa, *Ber.*, 41, 4472 (1908); M. A. Haller, *Compt. rend.*, 112, 446 (1896).

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