*The Reaction of cis-2-α-Carboxyethylcyclopentanol Lactone**

By Tsuguo TANAKA

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It is of some interest to synthesize nor-nepetalactone and nor-nepetalic acid through the stereospecific route starting from a compound of an identified structure. The author attempting such a synthesis, has examined some reactions of *cis*-2-α-carboxyethylcyclopentanol lactone[1].

First, in order to obtain cyanoacid III, *cis*-2-α-carboxyethylcyclopentanol lactone (I) was heated with potassium cyanide[2] at 250∼260°C for 24 hr., and the products were isolated and fractionally distilled. Two compounds were obtained as the main products. One was a lactone, $C_8H_{12}O_2$ (II), and the other, a cyanoacid, $C_9H_{13}O_2N$ (III). Many differences were observed between the infrared spectra as well as the ultraviolet spectra of lactone II and those of *cis*-2-α-carboxyethylcyclopentanol lactone I, although the molecular formulas of these two lactones are identical.

The 5.83 μ band of the carbonyl stretching vibration of II, as compared with the 5.70 μ band of that of I[1], seems to indicate that the five-membered γ-lactone ring of I is expanded to a six-membered δ-lactone ring[3] linked to the same cyclopentane unit, producing structure (II) of *cis*-3-α-carboxyethylcyclopentanol lactone as a result of the rearrangement[4] induced by potassium cyanide. Lactone II is easily hydrolysed by aqueous sodium hydroxide into the hydroxyacid, which is easily reconverted into the original lactone on acidification. We are dealing with *cis*-lactone in this case. In order to obtain further evidence for structure II, lactone II was hydrolysed with a 10% aqueous sodium hydroxide solution and the sodium salt of hydroxyacid was thoroughly oxidised with potassium permanganate. Two compounds were isolated from the reaction mixture. The one, a tricarboxylic acid, $C_8H_{12}O_6$ (IV), (m. p., 180°C), was identified as α-methyl-β-carboxyadipic acid[5] both by mixed melting point determination and by its infrared spectra, substantially supporting structure II for new lactone. The other, a tricarboxylic acid, $C_8H_{12}O_6$ (m. p., 140°C), was not identified. It might be the lower melting modification of α-methyl-β-carboxyadipic acid, but its identity was not examined because the author could not convert α-methyl-β-carboxyadipic acid (m. p., 180°C[5]) into an acid of m. p. 140°C, either by heating the aqueous solution at 200°C for 10 hr. or by heating it in acetyl chloride[6]. Another possibility is β-(α-carboxyethyl)glutaric acid[7]. But mixed melting of tricarboxylic acid V with it shows a melting point depression.

In order to see whether or not there exists another modification of β-(α-carboxyethyl)-glutaric acid, the synthesis of this acid was attempted.

The condensation of diethyl β-bromoglutarate with diethyl methylmalonate produced diethyl glutaconate (VI) and tetraethyl 2, 3-bis(carboxymethyl)adipate (VII) ; the latter on hydrolysis yielded tetracarboxylic acid (m. p., 203°C) which was proved to be 2, 3-bis(carboxymethyl)adipic acid (VIII), reported previously to have been obtained from diethyl β-bromoglutarate by a different procedure[8]. Another condensation of diethyl malonate with diethyl β-bromoglutarate resulted in the same products. The original aim was no attained. The hydrolysis of cyanoacid III with hydrochloric acid yielded a dicarboxylic acid, $C_9H_{14}O_4$ (IX) (m. p., 130°C).

Cyanoacid III was treated with oxalyl chloride and warmed on the water bath. The cyanoacid chloride X obtained was, very unstable. The distillation of the raw material was accompanied by extensive degradation and resinification and was not considered to be an convenient intermediate for further synthesis.

In the second scheme, attention was centered on the reduction of *cis*-lactone I into hydroxyaldehyde (XII).

The reduction of *cis*-lactone I with lithium

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* The Synthesis of Cyclopentane Derivatives. II. Parts of this paper were presented in a preliminary way in This Bulletin, **34**, 888 (1961).

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

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

[3] L. J. Bellamy, "Infrared Spectra of Complex Molecules," Methuen, London (1954), pp. 153, 159; R. N. Jones, P. Humphries and K. Dobrıner, *J. Am. Chem. Soc.*, **72**, 956 (1950) ; G. Stork and R. Breslow, ibid., **75**, 3291 (1953).

[4] Cf. C. C. Price and W. Kaplan, ibid., **66**, 477 (1944).

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

[6] A. Küster, *Ann.*, **345**, 39 (1906).

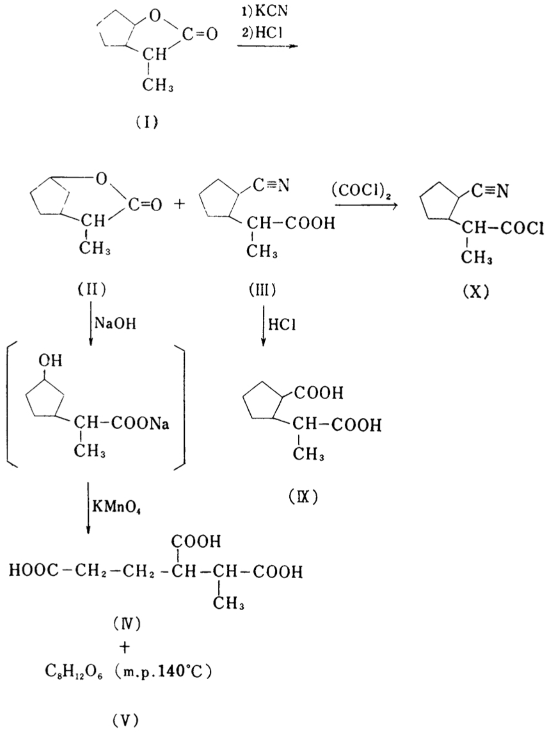
[7] Z. H. Skraup, *Monatsh.*, **21**, 1907 (1900).

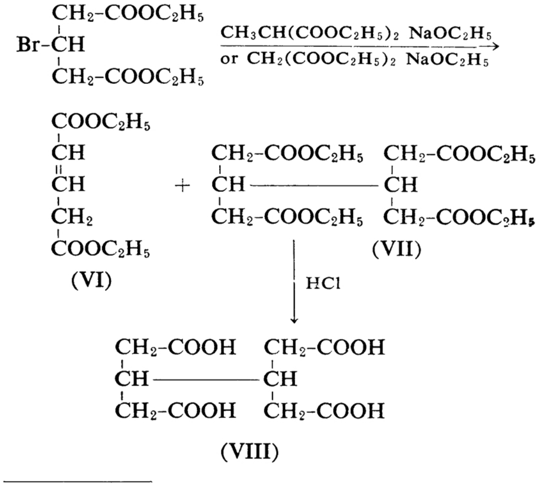
[8] Ch. Grundmann and H. Paul, *Ber.*, **86**, 186 (1953); C. T. Blood, N. J. Cartwright and R. P. Linstead, *J. Chem., Soc.*, **1952**, 2268.

aluminum hydride at a low temperature[9] was not satisfactory. It is liable to produce diol (XIII) and unreacted recoveries. The reduction of methylanilide of hydroxyacid XI with lithium aluminum hydride[10] is also a possible route to a hydroxyaldehyde. It is realized in this case that the reduction of methylanilide XI proceeds in as much as a 50~55% yield. However, the yield of the methylanilide in the reaction of *cis*-lactone with methylanilinomagnesium bromide[11] as well as with methylanilinomagnesium iodide is not satisfactory. When the *cis*-lactone is treated with an equivalent amount of a fresh colorless reagent (immediately after methylaniline has been added), plates (m. p., 130°C (a)) are obtained in a low yield but in a very pure state. However, in the usual procedures using an excess amount of an aged (20 min.), purple-colored methylanilinomagnesium bromide solution, although the yield is improved the products are crystal needles (m. p., 110~120°C) from which, after repeated crystallization from ethyl acetate, a lower yield of crystals (m. p., 130°C (a)) is obtained. The chromatography of a tetrahydrofuran solution of crystals (m. p., 110~120°C) through alumina produced in a 64% yield, crystals (m. p., 130°C (b)), the 14.14 μ band of the infrared spectra of which differs from the corresponding 14.35 μ band of that of crystal with a m. p. of 130°C (a) although the mixed melting of these two methylanilides does not show any melting point depression.

The configuration of the carbon atom adjacent to the carbonyl group of *cis*-lactone I is considered to be that formulated by Ia, whereas for *trans*-2-α-carboxyethylcyclopentanol lactone, either XIVa or XIVb is possible. In accordance with this, the singlet infrared band (10.50; 11.13 μ) of *cis*-lactone appears as a doublet band (10.50, 10.64; 11.13, 11.25 μ) of *trans*-lactone[1]. However, whether or not modifications a and b correspond to XIa and XIb respectively has not been ascertained. It seems probable that the colorless methylanilinomagnesium bromide which is produced immediately by reacting the ethylmagnesium bromide with methylaniline is a covalented $C_6H_5(CH_3)$-N-MgBr and that the aged, purple-colored solution of the reagent is an ionic conjugate, $C_6H_5(CH_3)N^{\ominus}Mg^{\oplus}Br[O(C_2H_5)_2]_2$ which is an effective reagent for the aldol type condensation[12] and which can also act to induce the dissociation of the hydrogen attached to the carbon atom adjacent to the carbonyl group, resulting in the inversion or racemization at a carbon atom adjacent to the carbonyl. For methylanilinomagnesium iodide, however, no such ionic conjugate form seems possible.

By the reaction of hydroxyaldehyde XII with ethylene glycol a high yield to product is obtained, although it is not the ordinary form of the ethylenedioxy derivative but a cyclic acetal formulated in XV[9b].





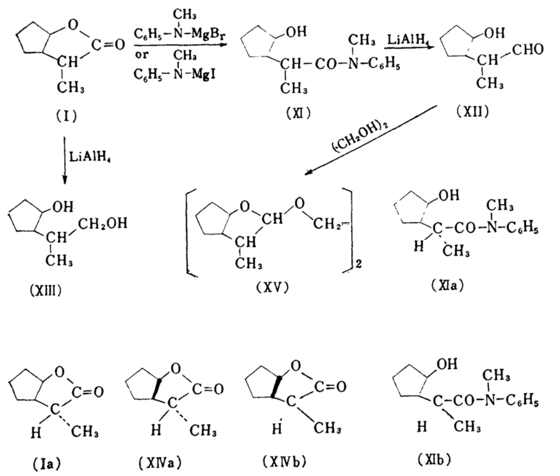
9a) Cf. G. E. Arth, *J. Am. Chem. Soc.*, **75**, 2413 (1953).

9b) Cf. H. Ohara, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **82**, 65 (1961).

10) F. Weygand, G. Eberhardt, H. Linden, F. Schäfer and I. Eigen, *Angew. Chem.*, **65**, 525 (1953).

11) Cf. F. Bodroux, *C. r. d. l'Acad. des Sciences*, **138**, 1427 (1904).

12) A. T. Nielsen, C. Gibbons and C. A. Zimmermann, *J. Am. Chem. Soc.*, **73**, 4696 (1951); W. G. Garden and F. D. Gunstone, *J. Chem. Soc.*, **1952**, 2651.



Experimental

***cis*-3-α-Carboxyethylcyclopentanol Lactone (II) and 2-α-Carboxyethylcyclopentyl Cyanide (III).**—Eight grams of *cis*-2-α-carboxyethylcyclopentanol lactone (I) and 6.4 g. of potassium cyanide are sealed in a glass tube and heated at 250~260°C for 24 hr. The mass becomes a dark solid. After cooling, the tube is opened (a slight pressure is observed) and the reaction mass is dissolved in 60 ml. of water. When 10 ml. of 6 N hydrochloric acid is added to the solution, it becomes turbid and some tarry substance separates. The suspension is made alkaline by the addition of an excess of a saturated sodium bicarbonate solution, and a small amount of active charcoal is added and filtered. The tarry residue is further extracted with a sodium bicarbonate solution. The filtrates are joined and acidified with 30 ml. of concentrated hydrochloric acid and extracted with ether. The ether layer is separated and washed with water. Ethereal solutions obtained from six batches of such a reaction (treating 48 g. of *cis*-lactone) are joined and then dried with sodium sulfate. The ether is evaporated, and the residue is distilled in a vacuum. Two fractions are obtained as the main distillate.

Fraction 1: 15 g. of oil (b. p., 48~85°C/3 mmHg), the redistillation of which gives 13 g. of the fraction (b. p. 85~86°C/3.5 mmHg). Yield, 27.1%. $\lambda_{\max}^{\mathrm{EtOH}}$ 211 mμ, IR 5.83 μ (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%.

Fraction 2: 11 g. of oil (b. p., 126~127°C/0.6 mmHg. Yield, 22.9%. $\lambda_{\max}^{\mathrm{EtOH}}$ 212.5 mμ, IR 5.84 μ (C=O), 4.42 μ (C≡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%.

Oxidation of *cis*-3-α-Carboxyethylcyclopentanol Lactone (II) with Potassium Permanganate.—To a stirred and ice-cooled solution of 3g. of lactone (II) dissolved in aqueous sodium hydroxide (1.1 g. sodium hydroxide in 9 ml. water), a saturated aqueous solution of 12 g. of potassium permanganate is added for 30 min.; the mixture is then left to stand overnight. Copious precipitates of manganese dioxide are filtered out, and the mother liquor is evaporated to a syrup, acidified with concentrated hydrochloric acid, and evaporated to dryness; the residue is then extracted with ether. Evaporation of the ether produces crystals (m. p., 120°C) which are dissolved in ethyl acetate and precipitated by adding petroleum ether. The procedure is repeated again, and the precipitate thus obtained is recrystallized twice from ethyl acetate. M. p., 140°C. 300 mg. Melting point depression was observed by mixed melting with authentic β-(α-carboxyethyl)-glutaric acid synthesized by the method of Skraup[7]. IR 5.86, 5.81 (shoulder) μ (C=O)[13].

Found: C, 47.26; H, 6.21. Calcd. for $C_8H_{12}O_6$: C, 47.06; H, 5.92%.

The filtered manganese dioxide is extracted three times with 100 ml. of a 3% aqueous sodium hydroxide solution. The combined filtrates are evaporated to a syrup, acidified with concentrated hydrochloric acid and evaporated to dryness. The residue is extracted with ether; the evaporation of ether from the ether extract produces crystals with a m. p. of 160°C which, after recrystallization twice from ethyl acetate, give crystals with a m. p. of 180°C, the mixed melting of which with authentic α-methyl-α-β-carboxyadipic acid does not show any melting point depression; also the infrared spectra of this acid is superimposable with that of α-methyl-β-carboxyadipic acid synthesized by Perkin's method. IR 5.89, 5.83 (shoulder) μ (C=O).

Found: C, 47.05; H, 6.28. Calcd. for $C_8H_{12}O_6$: C, 47.06; H, 5.92%.

2-α-Carboxyethylcyclopentanecarboxylic Acid (IX).—One gram of cyanoacid III is dissolved in 7 ml. of concentrated hydrochloric acid and refluxed for 8 hr. Hydrochloric acid is evaporated on the water bath, and from the concentrated hydrochloric acid solution crystals separate out on cooling. Recrystallized from ethyl acetate. M. p., 130°C. Yield, 150 mg.

Found: C, 57.77; H, 7.62. Calcd. for $C_9H_{14}O_4$: C, 58.05; H, 7.58%.

α-(2-Cyanocyclopentyl)propionic Acid Chloride (X).—Three grams of cyanoacid III, 3.5 g. of oxalyl chloride and 6 ml. of benzene are mixed and refluxed on the water bath for 2 hr. Benzene and excess oxalyl chloride are evaporated off, and the residue is distilled in vacuum. 2.1 g. of the fraction with a b. p. of 90~105°C/3 mmHg is obtained, from which on redistillation there emerges a fraction with a b. p. of 96.5~99.5°C/0.6 mmHg. IR 5.60, 5.91 μ (C=O); 4.44 μ (C≡N).

Found: C, 58.63; H, 6.49; N, 5.76. Calcd. for $C_9H_{12}ONCl$: C, 58.22; H, 6.52; N, 7.55%.

Tetraethyl 2,3-Bis(carboxymethyl)adipate (VII).—(1) 0.7 g. of sodium is dissolved in 25 ml. of absolute alcohol, to which after cooling is added 5.2 g. of diethyl methylmalonate. The solution is stirred and kept at 20°C, and 8 g. of diethyl-β-bromoglutarate is added to it over the period of

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[13] Those of synthetic β-(α-caboxyethyl)glutaric acid are 5.73, 5.87 and 5.95 (shoulder) μ. Many differences are observed between the infrared spectra of the acid (m. p., 140 C°) isolated and those of β-(α-carboxyethyl)glutaric acid and α-methyl-β-carboxyadipic acid.

an hour. Stirring is continued at 20°C for an hour more, and then the solution is refluxed on a water bath for an hour. The alcohol is distilled off, the reaction mixture is poured into ice-water, and the product is extracted with ether. The ether layer is washed with water and dried with sodium sulfate. The ether is distilled off, and the residue is distilled in vacuum. Three fractions are obtained. Fraction I. B. p., 60°C/2.5 mmHg (obtained by redistillation of the fraction with a b. p. of 63~120°C/4 mmHg). 3.6 g. Diethyl methylmalonate. By reaction with ammonia, it gives methylmalonamide (m. p., 206°C). Fraction II, B. p., 83~85°C/2.5 mmHg (obtained by redistillation of the fraction with a b. p. of 63~120°C/4 mmHg). Diethyl glutaconate. IR 5.8 μ (C=O), 6.05 μ (C=C), 2.90 μ (very weak, OH)[14].

Found: C, 57.74; H, 7.71. Calcd. for $C_9H_{14}O_4$: C, 58.05; H, 7.58%. Fraction III. B. p., 155~165°C/2.5 mmHg. 2.4 g. Tetraethyl 2, 3-bis(carboxymethyl)adipate.

Found: C, 57.77; H, 7.83. Calcd. for $C_{18}H_{30}O_8$: C, 57.74; H, 8.08%.

(2) 0.6 g. of sodium is dissolved in 17 ml. of absolute alcohol, to which is added 4.2 g. of diethyl malonate. The solution is stirred and cooled in an ice bath, and 7 g. of diethyl β-bromoglutarate is added to it over a 30-min. period. After the addition is over, stirring is continued for 2.5 hr.; then the solution is refluxed on a water bath for 2 hr. more. After cooling, the reaction mixture is poured into ice-water and dried with sodium sulfate. The ether is distilled off, and the residue on distiliation in vacuum yields three fractions. Fraction I. B. p., 60~65°C/2.5 mmHg. 4 g. Diethyl malonate. By reaction with ammonia it gives malonamide (m. p., 168°C). Fraction II. B. p., 82~85°C/2.5 mmHg. 2.3 g. Identified as diethyl glutaconate by comparison of infrared spectra. Fraction III. B. p., 153~155°C/2.5 mmHg. 1 g. Tetraethyl 2, 3-bis(carboxymethyl)adipate.

Found: C, 57.87; H, 7.89. Calcd. for $C_{18}H_{30}O_8$: C, 57.74; H, 8.08%.

2, 3-Bis(carboxymethyl)adipic Acid (VIII).—Two grams of tetraester VII is mixed with 18 ml. of concentrated hydrochloric acid and refluxed for 10 hr. After evaporation of the hydrochloric acid and cooling, crystals separate out which are three times recrystallized from ethyl acetate. M. p., 203°C. On further recrystallization from acetone, it shows a m. p. of 206°C. Yield, 200 mg.

Found: C, 45.92; H, 4.99. Calcd. for $C_{10}H_{14}O_8$; C, 45.80; H, 5.38%.

Diethyl β-Bromoglutarate.—7.2 g. of β-bromoglutaric acid[15], 36 ml. of absolute alcohol and 1.8 g. of concentrated sulfuric acid are mixed and refluxed for 5 hr. Thirty milliliters of benzene is added to it, the benzene and alcohol are distilled off, and the residue is poured into ice-water and extracted with ether. The ether layer is separated, washed with an aqueous sodium bicarbonate solution and water, dried with sodium sulfate, and distilled. B. p., 114~115°C/2.5 mmHg. 7.3 g.

Found: C, 40.67; H, 5.84. Calcd. for $C_9H_{15}O_4Br$: C, 40.46; H, 5.66%.

Reduction of *cis*-Lactone I with Lithium Aluminum Hydride.—Twenty-one grams of *cis*-lactone I is dissolved in 40 ml. of tetrahydrofuran and cooled to −15~−13.5°C, while 1.8 g. of lithium aluminum hydride dissolved in 60 ml. of tetrahydrofuran is efficiently stirred in at this temperature over a 40-min. period. Stirring is continued at that temperature for 30 min., and then the solution is left to stand to raise the temperature to 7°C. The reaction mixture is poured into ice-colled aqueous hydrochloric acid (concentrated hydrochloric acid 110 ml. in 200 ml. of water), and extracted with ether. The ether layer is separated, washed with water, and dried with sodium sulfate. The ether is distilled off and, on fractionation of the residue, the following fractions are obtained. Fraction I. B. p., 72~82°C/5.5 mmHg. 0.2 g. Fraction II. 82~89°C/5.5 mmHg. 3.8 g. The infrared spectra of these fractions show a band of 2.98 μ (OH stretching), but it lacks many of the characteristic bands of hydroxyaldehyde XII and is considered to be an unreacted lactone contaminated with some hydroxylic compounds. Fraction III. B. p., 89~93°C/5.5 mmHg. Recovered lactone. Fraction IV. B. p., 132~135°C/3 mmHg. 6 g. *cis*-Diol XIII.

Methylanilide of *cis*-2-α-Carboxyethylcyclopentanol (XI).—Into a solution of ethylmagnesium bromide (prepared by the reaction of 48 g. of magnesium with 24 g. of ethyl bromide in 200 ml. of ether) is efficiently stirred a solution of 18.2 g. of methylaniline in 50 ml. of ether (nitrogen atmosphere; moisture is avoided) over a 10-min. period in an ice bath. After stirring is continued for 25 min., a deep purple solution of methylanilinomagnesium bromide is produced, to which is added 11 g. of *cis*-lactone I in 50 ml. ether for 5 min. The ice bath is removed, and the reaction mixture is refluxed for one and a half hours with stirring. After the reaction is over, the mixture is cooled in an ice bath and decomposed by the addition of dilute hydrochloric acid (30 ml. of concentrated hydrochloric acid in 300 ml. of water). The products are thoroughly extracted with ether, and the ether layers are separated, washed with an aqueous sodium bicarbonate solution and water, and dried with sodium sulfate. The ether is distilled off, and the residue, which separates as a yellow solid, is washed with a small amount of ethyl acetate. Crystals with a m. p. of 110°C are obtained. Yield, 11 g. After recrystallization six times from ethyl acetate, 3.2 g. of plates (m. p., 130°C) are obtatined. IR 6.18 μ (C=O), 2.99 μ (OH).

Found: C, 72.75; H, 8.52; N, 5.66. Calcd. for $C_{15}H_{21}O_2N$: C, 72.84; H, 8.56; N, 5.66%.

From the mother liquor, needles with a m. p. of 110~118°C are obtained.

Found: C, 72.72; H, 8.48; N, 5.76. Calcd. for $C_{15}H_{21}O_2N$: C, 72.84; H, 8.56; N, 5.66%.

In an analogous procedure using 12 g. of *cis*-lactone I, 9.8 g. of methylaniline, 2.4 g. magnesium and 12 g. of ethylbromide, 9.8 g. of raw crystals with a m. p. of 110°C are obtained; from these, after repeated recrystallization from ethyl acetate, 4.6 g. of

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14) F. Henrich, *Ber.*, **35**, 1663 (1902).

15) Obtained by the method of Semenow, *Chem. Zentr.*, **11**, 28 (1899).

plates (m. p., 130°C) are obtained. However, when the reaction is conducted in such a way as *cis*-lactone I is added to a fresh colorless methylanilinomagnesium bromide solution (immediately after methylaniline has been added), the yield of the raw methylanilide is 6.5 g.; from these, after one recrystallization from ethyl acetate, 4.8 g. of plates (m. p., 130°C) are obtained.

By the use of 6 g. of *cis*-lactone I, 11.5 g. of methylaniline, 2.5 g. of magnesium and 14.2 g. of methyl iodide, 4.4 g. of the raw methylanilide is obtained; after recrystallization from ethyl acetate this gives 2.8 g. of crystals with a m. p. of 130°C. Methylanilinomagnesium iodide consists of crystals insoluble in ether. A tetrahydrofuran solution of methylanilide with a m. p. of 110∼118°C is chromatographed on alumina. From an tetrahydrofuran effluent plates with a m. p. of 130°C are obtained in a 64% yield after one recrystallization from ethyl acetate. However, the 14.14 μ band of the infrared spectra of these plates differs from the 14.35 μ band of that of crystals with a m. p. of 130°C obtained by direct crystallization of the reaction product.

***cis*-2-α-Formylethylcyclopentanol** (XII).—11.5 g. of methylanilide of *cis*-2-α-carboxyethylcyclopentanol is dissolved in 110 ml. of tetrahydrofuran and cooled in an ice-salt bath. 1.1 g. of powdered lithium aluminum hydride is efficiently stirred into it for 30 min. After the addition is over, the ice-salt bath is replaced by an ice bath and stirring is continued for 7.5 hr. 200 ml. of hydrochloric acid (1 : 4) is added, the mixture is left to stand overnight and then extracted with ether. The ether layer is separated, washed with water and dried with sodium sulfate. The ether is distilled off, and the residue is distilled in vacuum. 3.5 g. of an oil b. p. 89∼90°C/5 mmHg are obtained. *cis*-2-α-Formyl ethylcyclopentanol. IR 2.93, 2.85 μ (OH), 5.70 μ (C=O).

Found: C, 68.00; H, 8.94. Calcd. for $C_8H_{14}O_2$: C, 67.57; H, 9.93%.

Ethylenedioxy Derivative XV.—Four grams of 2-α-formylethylcyclopentanol and 2.5 g. of ethyleneglycol, together with 20 mg. of *p*-toluenesulfonic acid, are dissolved in 15 ml. of benzene and refluxed for 3 hr. 50 ml. of benzene is gradually added while the amount of benzene and water formed in the reaction are distilled off over a 4-hr. period. After cooling, the reaction mixture is diluted with ether, washed with an aqueous sodium bicarbonate solution and water, dried with sodium sulfate, and distilled. 3.1 g. of an oil (b. p., 76∼78°C/3 mmHg) are obtained.

Found: C, 68.65; H, 8.86. Calcd. for $C_{18}H_{30}O_4$: C, 69.64; H, 9.74%.

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Faculty of Liberal Arts
Saga University
Honjo, Saga City

[*1] Present address: Shin Nihon-Chisso Fertilizers Company, Minamata, Kumamoto.

[*2] Present address: Faculty of Science, Kyushu University.