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Abstract

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δ-Lactones. Preparation of Acylated Butyrolactones from γ-Bromo-δ-Keto Acids

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In our previous communications (^{1,2}) a preparative method was described for obtaining γ-bromo-δ-keto acids by the interaction of dibromides of unsaturated δ-lactones with water; for example (^{2}):

$$\mathrm{CH_3\text{-unsaturated }\delta\text{-lactone}} \xrightarrow{\mathrm{Br_2}} \text{dibromide} \xrightarrow[-\mathrm{HBr}]{+\mathrm{H_2O}} \mathrm{CH_3COCH(Br)CH_2CH_2COOH}$$

In the present work it was shown that the γ-bromo-δ-keto acids obtained in this way, under the action of a saturated aqueous solution of sodium acetate in the cold, are converted into butyrolactones acylated in position 5.

By this reaction, from the corresponding γ-bromo-δ-keto acids, there were obtained in good yields 5-acetylbutyrolactone ((I), yield 60.5%), 5-acetyl-5-methylbutyrolactone ((II), 49.2%), the lactone of 2-hydroxy-2-(β-carboxyethyl)cyclopentanone ((III), 61.5%), the lactone of 2-hydroxy-2-(β-carboxyethyl)cyclohexanone ((IV), 56%), and the lactone of 2-hydroxy-2-(β-carboxyethyl)-tetralone-1 ((V), 71%):

$$\mathrm{CH_3COCH(Br)CH_2CH_2COOH} \xrightarrow[-\mathrm{HBr}]{\mathrm{CH_3COONa}} \text{5-acetylbutyrolactone} \qquad \text{(I)}$$

$$\mathrm{CH_3COC(Br)(CH_3)CH_2CH_2COOH} \xrightarrow[-\mathrm{HBr}]{\mathrm{CH_3COONa}} \text{5-acetyl-5-methylbutyrolactone} \qquad \text{(II)}$$

$$\text{2-bromo-2-(-carboxyethyl)cyclopentanone} \longrightarrow \text{lactone of 2-hydroxy-2-(-carboxyethyl)cyclopentanone} \qquad \text{(II}$$

$$\text{2-bromo-2-(-carboxyethyl)cyclohexanone} \longrightarrow \text{lactone of 2-hydroxy-2-(-carboxyethyl)cyclohexanone} \qquad \text{(IV)}$$

2-bromo-2-(-carboxyethyl)tetralone-1 ⟶ lactone of 2-hydroxy-2-(-carboxyethyl)tetralone-1 (V)

Thus, the reaction described can serve as a preparative method for obtaining acylated butyrolactones.

In all cases except the first, one might have assumed the formation, in addition to butyrolactones, of the isomeric saturated six-membered lactones (VII), if the reaction proceeded through the intermediate formation of unsaturated ketonic acids (VI), for example:

[structural scheme: bromoketonic acid] $\xrightarrow[-HBr]{CH_3COONa}$ [structural scheme: unsaturated ketonic acid (VI)] ⟶ [s

However, this assumption is not valid, since experiment showed that the specially synthesized unsaturated ketonic acid VI is not changed by the action of a saturated aqueous solution of sodium acetate. Substances I–V are not titrated by aqueous or alcoholic alkali solutions, do not decolorize bromine water, and give semicarbazones (except V).

The presence of the lactone ring in the compounds obtained was confirmed by converting one of them (V) into the corresponding γ-hydroxy acid. On heating lactone V with an aqueous solution of caustic soda and subsequent acidification, it was possible to obtain hydroxy acid (VIII), and from it, by the action of diazomethane, the methyl ester (IX); hydroxy acid VIII was readily converted into lactone V on heating, and the methyl ester of hydroxy acid IX–on heating or by the action, in the cold, of concentrated hydrobromic acid:

[structural scheme: lactone (V)] $\underset{\text{heating}}{\overset{\text{NaOH} \quad \text{HCl}}{\rightleftarrows}}$ [structural scheme: hydroxy acid (VIII)] $\xrightarrow{CH_2N_2}$ [structural sch

[structural scheme: methyl ester (IX)] $\xrightarrow[\text{or HBr}]{\text{heating}}$ [structural scheme: lactone (V)]

These reactions, as well as the analytical data, confirm the structure of the substances I–V obtained as acylated butyrolactones.

Experimental Part

5-Acetylbutyrolactone (I). 10 g of crystalline γ-bromo-γ-acetylbutyric acid (m.p. 39–41° (2)), 19.5 g of sodium acetate, and 20 ml of water were stirred in the cold for 2 hours; the reaction mixture was then extracted with ether (in an extractor) for 10 hours. 5-Acetylbutyrolactone (3.7 g, yield 60.5%) had the following constants: b.p. 143—144° at 15—17 mm, n_D^{20} 1.4630, d_4^{20} 1.1990, M_R 29.41. For $C_6H_8O_3$, calculated M_{RD} 29.37.

Found %: C 56.20; 55.75; H 6.67; 6.37
$C_6H_8O_3$. Calculated %: C 56.26; H 6.30

M.p. of the semicarbazone 180—181° (from alcohol).

Found %: N 22.69; 22.63
$C_7H_{11}O_3N_3$. Calculated %: N 22.69

Literature data (3): b.p. 113—116° at 10 mm, n_D^{20} 1.4657; d_4^{20} 1.222, M_{RD} 28.76. M.p. of the semicarbazone 184—185°.

5-Methyl-5-acetylbutyrolactone (II) was obtained by the same route from γ-bromo-γ-acetylvaleric acid (m.p. 79-80° (1)) in 49.2% yield: b.p. 119° at 13 mm, n_D^{20} 1.4600, d_4^{20} 1.1340, MR_D 34.34. For $C_7H_{10}O_3$, MR_D calculated 33.99.

Found, %: C 59.19; 59.37; H 7.18; 7.34
$C_7H_{10}O_3$. Calculated, %: C 59.17; H 7.08

M.p. of the semicarbazone 180.5° (from alcohol).

Found, %: N 21.10; 20.88
$C_8H_{13}O_3N_3$. Calculated, %: N 21.09

Literature data (4) (obtained by hydration of γ-ethynyl-γ-valerolactone): b.p. 115-116° at 10 mm; m.p. of the semicarbazone 182-183°.

Lactone of 2-oxo-2-(β-carboxyethyl)cyclopentane (III). 4 g of 2-bromo-2-(β-carboxyethyl)cyclopentanone (m.p. 55-56° (2)), 7 g of sodium acetate, and 8 ml of water were vigorously stirred for two hours; the crystals of the ketonolactone (III) formed were filtered off, washed with water, and dried (1.6 g; yield 61.5%): m.p. 105-106° (from ether).

Found, %: C 62.35; 62.23; H 6.50; 6.44
$C_8H_{10}O_3$. Calculated, %: C 62.36; H 6.54

Semicarbazone: m.p. 230° (with decomposition, from aqueous alcohol).

Found, %: N 19.99; 19.57
$C_9H_{13}O_3N_3$. Calculated, %: N 19.89

Lactone of 2-oxo-2-(β-carboxyethyl)cyclohexane (IV) was obtained in 56% yield from 2-bromo-2-(β-carboxyethyl)cyclohexanone (m.p. 70-71°) by the same method as lactone (III): b.p. 148-149° at 7 mm, m.p. 54-55° (from ether).

Found, %: C 64.36; 64.34; H 7.38; 7.34
$C_9H_{12}O_3$. Calculated, %: C 64.26; H 7.14

Semicarbazone: m.p. 200° (from alcohol, with decomposition).

Found, %: N 18.67; 18.85
$C_{10}H_{15}O_3N_3$. Calculated, %: N 18.66

Literature data (5) (obtained, along with other reaction products, by oxidation of the dimer of *o*-methylenecyclohexanone with subsequent treatment with alkali): m.p. 60°, m.p. of the semicarbazone 196° (with decomposition).

Lactone of 2-oxo-2-(β-carboxyethyl)-tetralone-1 (V). 6 g of 2-bromo-2-(β-carboxyethyl)-tetralone-1 (m.p. 143°), 12 g of sodium acetate, 15 ml of water, and 3 ml of alcohol were stirred for one hour and left overnight. The crystals that separated from the solution after evaporation of the alcohol were washed with water and dried. The ketonolactone V obtained melted at 100–101° (from benzene).

Found, %: C 72.54; 72.65; H 5.74; 5.75
$C_{13}H_{12}O_3$. Calculated, %: C 72.22; H 5.55

It was not possible to obtain the semicarbazone of ketonolactone V under ordinary conditions.

2-Oxo-2-(β-carboxyethyl)-tetralone-1 (VIII). 4 g of ketonolactone V was dissolved in 10 ml of 10% aqueous sodium hydroxide solution with slight heating. To the resulting solution, upon cooling, concentrated hydrochloric acid was added dropwise. The precipitated keto acid VIII (3.9 g), washed with distilled water and dried in a vacuum desiccator, melted at 116–117° (the melting point was determined in an apparatus preheated to 110°).

Found, %: C 66.48; 66.55; H 6.07; 6.10
$C_{13}H_{14}O_4$. Calculated, %: C 66.66; H 5.98

Upon crystallization from alcohol, the resulting hydroxy acid VIII was converted partially, and upon distillation completely, into the initial ketolactone V (mp 100°).

2-Oxy-2-(β-carbethoxyethyl)-tetralone-1 (IX). To 3.8 g (0.017 mole) of hydroxy acid VIII were added 36 ml of an ethereal solution containing ~0.03 mole of diazomethane. After completion of the reaction, the ether was evaporated in vacuo; the remaining oil crystallized on prolonged standing: mp 42–42.5°. When an attempt was made to recrystallize the obtained hydroxy-acid ester from alcohol, as well as upon its distillation or treatment with concentrated hydrobromic acid in the cold, ketobutyrolactone V (mp 100°) was formed in quantitative yield.

Attempted lactonization of the unsaturated keto acid (VI). The unsaturated keto acid (VI)* (mp 75-76°; semicarbazone mp 180–181°) was treated with an aqueous solution of sodium acetate under the same conditions as 2-bromo-2-(β-carboxyethyl)cyclohexanone. From the reaction mixture the initial acid VI was isolated, mp 75°. The semicarbazone had mp 180°; a mixed sample with the semicarbazone of the initial unsaturated keto acid melted without depression.

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* The synthesis and transformations of this unsaturated δ-keto acid will be described in the following communication.

Note: Figure translations are in progress. See original paper for figures.

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