

Reaction of γ, γ -Dimethyl- α, β -dicarbethoxybutyrolactone with Acetyl Chloride¹⁾

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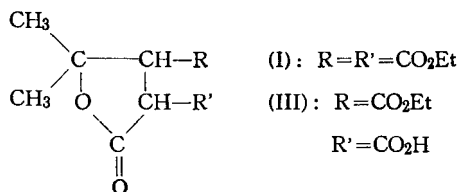
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Acetylation of γ, γ -dimethyl- α, β -dicarbethoxybutyrolactone in benzene in the presence of sodium hydride was attempted. The structure of the condensation product was assigned to O-acetyl derivative, which was converted into γ, γ -dimethyl- β -carbethoxy- α -carboxybutyrolactone whose structure is also discussed by IR spectrum.

Although alkylation of α -position of α -carbethoxybutyrolactones has been reported,^{2), 3)} similar attempt to prepare complex material such as the title compound has not appeared in literature. The authors were interested in examining the reactivity of α -hydrogen atom of α, β -dicarbethoxybutyrolactone system^{4), 5), 6), 7)} in order to discover a new route to α -substituted butyrolactones. In this paper the reaction of γ, γ -dimethyl- α, β -dicarbethoxybutyrolactone (I) with acetyl chloride in the presence of sodium hydride in benzene solution is described.

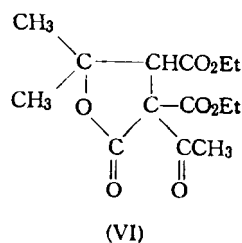
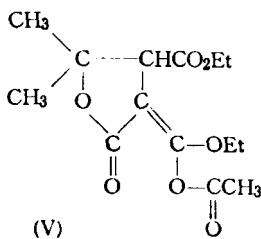
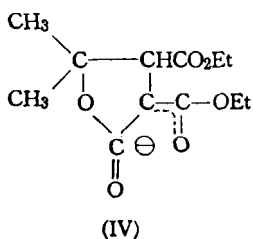
The acetylation was carried out in benzene solution by heating equimolar amount of the dicarbethoxybutyrolactone (I) with acetyl chloride. The condensation product (II) has new absorption bands at 1715, 1355, 1125, and 1060 cm^{-1} , showing the presence of acetyl group. Elemental analysis also supported the formula of $\text{C}_{14}\text{H}_{20}\text{O}_7$. Hydrolysis of II with 1*N* alkaline solution under reflux gave γ, γ -dimethylparaconic acid⁸⁾, and when treated at room temperature, γ, γ -dimethyl- β -carbethoxy- α -carboxybutyrolactone (III) was separated in a quantitative yield. Furthermore, II decomposed in the moist air gradually into I and acetic acid. The struc-



ture of the α -carboxybutyrolactone (III) was confirmed by converting into anilide, methyl ester, and the corresponding ethyl paraconate⁹⁾.

Discussion

It would seem generally observed that in the reaction of enolate anion O-acylation occurs by the use of aprotic solvents or O-alkylation by treating with an alkylating agents having nature of carbonium ion¹⁰⁾. Although ambident anion of α -carbethoxybutyrolactone has not been reported, it seems possible that the reaction of the anion (IV) may proceed in enol form when treated with acetyl chloride in benzene solution. The facile interconversion between I and II and the enhancement of the absorption band at 1375 cm^{-1} owing to enol acetate¹¹⁾ appear to be due to more unstable structure (V), i. e., O-acetyl compound, in comparison with the structure of VI. The behaviours of the ambident anion of α -



acetylbutyrolactone in different solvents have been reported¹²). It is to be noted that O-alkylation occurs in xylene in contrast to C-alkylation in mixed solution of ethanol and ether. Thus, in view of the solvent effect and the species of

the reagent the title reaction may be expected to proceed by the O-acetylation.

The IR spectrum of the lactone carboxylic acid (III) shows complex absorption bands in the carbonyl region as shown in Figure 1, since two

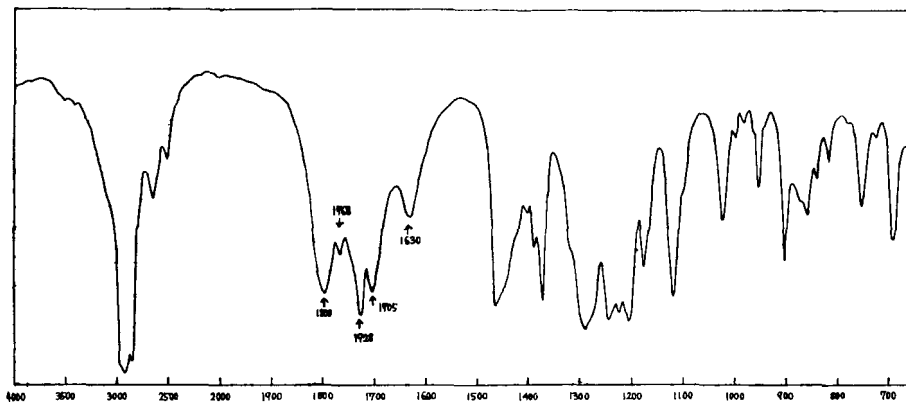


Fig. 1. γ, γ -Dimethyl- β -carbethoxy- α -carboxybutyrolactone (III)

unexpected bands at 1800 and 1630 cm^{-1} are observable; the former may be due to lactone carbonyl and the latter due to enolated β -diketone system. On the other hand, the spectrum estimated in methanol solution has only two bands in the carbonyl region at 1770 cm^{-1} for lactone carbonyl and at 1735 cm^{-1} together with a shoulder at 1710 cm^{-1} for ester and carboxy carbonyls, and the methyl ester of III has also two bands at 1765 and 1735 cm^{-1} for lactone and ester carbonyls, respectively. From the above evidence, it might be considered that the structure of the lactone carboxylic acid (III) may be affected by the hydrogen bonding of the carboxyl group and the shift of the lactone carbonyl band to 1800 cm^{-1} may be due to the lactone ring strain.

Experimental¹³

Acetylation of γ, γ -Dimethyl- α, β -dicarbethoxybutyrolactone. — To a mixture of 5.9 g. (0.025 mole) of γ, γ -dimethyl- α, β -dicarbethoxybutyrolactone (I) and 1.2 g. (0.025 mole) of sodium hydride in 20 ml. of dry benzene 1.8 g. (0.05 mole) of acetyl chloride was added by stirring for 4 hours. The mixture was hydrolyzed with a saturated aqueous ammonium chloride solution and then extracted with ether, washed with water, and dried. The solvent was removed *in vacuo*. The residue was distilled to give 2.2 g. of acetylated compound,

b. p. 146–8°/3mm.; IR, 1775 cm^{-1} (lactone ν C=O), 1775 cm^{-1} (ester ν C=O), 1720 cm^{-1} (acetyl ν C=O, shoulder).

Anal. Calcd. for $\text{C}_{14}\text{H}_{20}\text{O}_7$: C, 55.99; H, 6.71. Found: C, 55.91; H, 6.82.

Decomposition of the acetylated compound (II) occurred spontaneously, when exposed to the moist air, to give crystalline γ, γ -dimethyl- α, β -dicarbethoxybutyrolactone (I) and acetic acid. These products were identified by infrared spectra in comparison with those of authentic samples.

Hydrolysis of the Acetylated Compound (II) with 1 N Alkali. Method A. — A mixture of 15 ml. of 1 N sodium hydroxide solution and 2.86 g. (0.01 mole) of the acetylated compound (II) obtained from the above procedure in 40 ml. of ethanol was stirred for 4 hours at room temperature and acidified to pH 7–6.5 with dilute sulfuric acid. The white precipitates were filtered and washed with water. On recrystallization from water, 2.15 g. (91%) of γ, γ -dimethyl- β -carbethoxy- α -carboxybutyrolactone (III), m. p. 136–136.5° (from water), was obtained.

Anal. Calcd. for $\text{C}_{10}\text{H}_{14}\text{O}_6$: C, 52.17; H, 6.13. Found: C, 52.35; H, 6.23.

Decarboxylation was carried out by heating the α -carboxybutyrolactone (III) at 120° for 1 hour to afford ethyl γ, γ -dimethylparaconate, b. p. 146°/15 mm., whose infrared spectra were superimposable in fine details with those of the

authentic sample⁹).

Method B. — Hydrolysis of the acetylated compound (II) with alkaline solution was carried out as described in the preceding paragraph, by refluxing for 4 hours. The resulted solution was acidified with dilute sulfuric acid. The organic layer was taken up in ether, washed with water and dried. The solvent was removed under diminished pressure. The residue, on recrystallization from toluene, gave γ,γ -dimethylparaconic acid, m. p. 173° (from alcohol). The infrared spectra of this terebic acid were identical with those of the authentic sample⁸).

Derivatives of the γ,γ -Dimethyl- β -carbethoxybutyrolactone.

Methyl Ester. — The above lactone acid (III), after esterification with diazomethane, was converted into the corresponding γ,γ -dimethyl- β -carbethoxy- α -carbomethoxybutyrolactone, b. p. 138°/3 mm.: IR, 1775 cm⁻¹. (lactone ν C=O) and 1730 cm⁻¹. (ester ν C=O).

Anal. Calcd. for C₁₁H₁₆O₆: C, 54.09; H, 6.60. Found: C, 53.73; H, 6.66.

Anilide. — To a mixture of 2.3 g. (0.011 mole) of γ,γ -dimethyl- β -carbethoxy- α -carboxybutyrolactone, 1 ml. of pyridine, and 0.7 ml. of thionyl chloride 1.4 g. (0.015 mole) of aniline was added under stirring for 4 hours. The mixture was hydrolyzed with water and taken up in ether. The ether solution was washed with sodium bicarbonate solution, with water and dried over anhydrous sodium sulfate. The solvent was removed *in vacuo*. On recrystallization from

benzene there was obtained γ,γ -dimethyl- β -carbethoxy- α -N-phenylamidobutyrolactone in a quantitative yield, m. p. 118.5°; IR, 3350 cm⁻¹ (ν NH), 1757 cm⁻¹ (lactone ν C=O), 1720 cm⁻¹ (ester ν C=O), 1670 cm⁻¹ (CONH ν C=O), and 1535 cm⁻¹ (δ NH).

Anal. Calcd. for C₁₆H₁₉O₅N: C, 62.94; H, 6.27; N, 4.59.

Found: C, 63.39; H, 6.31; N, 4.43.

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