SYNTHESIS OF 3,3,6,6-TETRAMETHYL-1,4-DIOXANE-2,5-DIONE

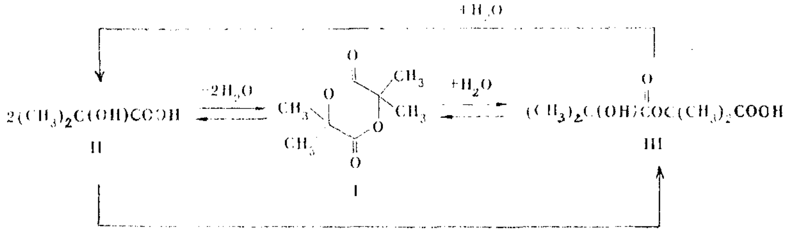
E. N. Zil'berman, V. N. Salov,
V. V. Leshin, and N. B. Matin

UDC 547.472.4'841:542.953.2

Conditions for the preparation of 3,3,6,6-tetramethyl-1,4-dioxane-2,5-dione by condensation of 2-hydroxy-2-methylpropanoic acid in the presence of p-toluenesulfonic acid were found. It is shown that the lactide obtained is readily hydrolyzed to 2-(2-hydroxy-2-methylpropanoyloxy)-2-methylpropanoic acid.

In order to obtain 3,3,6,6-tetramethyl-1,4-dioxane-2,5-dione (I), which is used as a monomer, one starts from 2-hydroxyisobutyric acid (II), which is heated in toluene in the presence of p-toluenesulfonic acid as the dehydrating agent [1]. However, when we attempted to reproduce the synthesis, instead of I, which has mp 79°C, we obtained a substance with mp 105°C, which was identified as 2-(2-hydroxy-2-methylpropanoyloxy)-2-methylpropanoic acid (III), as well as starting acid II. The quantitative determination of water in the condensation of acid II in combination with chromatographic analysis of the reaction mixture showed that under the conditions proposed in [1], one molecule of water is liberated for each molecule of acid II, and the reaction product is the expected dioxane I. However, during subsequent workup of the reaction mixture with water and a solution of sodium carbonate as specified by the method in [1], the percentage of dioxane I decreases sharply. It was established that dioxane I, which is insoluble in water, undergoes hydrolysis in a solution of alkali (0.1 mole/liter) in 1-2 min to give III, which also underwent hydrolysis, but to a lesser degree: It undergoes 100% hydrolysis in the cold 3 h after dissolving in a solution of alkali (0.1 mole/liter). The ease of hydrolytic destruction of dioxane I should be regarded as completely regular, since it is known [2] that other lactides also undergo hydrolysis readily at room temperature in acidic and alkaline media. The considerably lower hydrolytic stability of the ester group in dioxane I and other lactides as compared with ordinary esters can be explained by the fact that the heterorings in lactides are strained, and, consequently, their decomposition is energically favorable. This assumption is confirmed by the ability of lactides to undergo polymerization to give linear polymers [1, 3]. The greater resistance to the action of aqueous solutions of alkalis of the ester groups in acid III than in dioxane I also constitutes evidence in favor of this.

Thus the following transformations take place under the conditions of the synthesis of heterocyclic compound I:



The synthesis of dioxane I in high yield was possible owing to the exclusion of treatment of the reaction mixture with water and a solution of sodium carbonate and distillation of the reaction product *in vacuo*. Conditions for the synthesis and isolation of acid III were also established.

Dzerzhinsk Branch, A. A. Zhdanov Gorky Polytechnic Institute. Dzerzhinsk 606000. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 906-907, July, 1983. Original article submitted October 19, 1982.

EXPERIMENTAL

3,3,6,6-Tetramethyl-1,4-dioxane-2,5-dione (I). A mixture of 18.7 g (0.18 mole) of acid II, 1.8 g (0.01 mole) of p-toluenesulfonic acid, and 67 ml of toluene was refluxed with a Dean–Stark trap for 60 h (chromatographic monitoring of the decrease in the amount of acid II), after which the toluene was removed from the reaction mixture by distillation *in vacuo* (13.3 hPa); then, at the same pressure and a temperature of 106-108°C, 10.1 g (65%) of white crystals of individual (according to GLC data) dioxane I with mp 78°C (mp 79°C [1] and 71°C [4]) were obtained. PMR spectrum ($CDCl_3$): 1.40 (s, 6H) and 1.55 ppm (s, 6H).

2-(2-Hydroxy-2-methylpropanoyloxy)-2-methylpropanoic Acid (III). A) A stream of air was passed at room temperature through a cooled reaction mixture obtained as described above until crystals precipitated; 2 ml of water was added to the crystals, and the resulting pasty mass was recrystallized from petroleum ether (bp 60-80°C) to give 10.6 g (62%) of III (needles) with mp 105°C [5]. PMR spectrum ($CDCl_3$): 1.40 (s, 6H), 1.55 (s, 6H), and 6.30 ppm (s, 1H, OH). Found: neutralization equivalent 190 and ester number 294. $C_8H_{14}O_5$. Calculated: neutralization equivalent 190 and ester number 295.

B) Water (10 ml) and 2.5 ml of a solution of sodium hydroxide (0.1 mole/liter) were added successively to 0.041 g of dioxane I, after which a stream of air was passed through the resulting solution, as in the preceding experiment, to give 0.056 g of the sodium salt of acid III, to which 2.7 ml of hydrochloric acid (0.1 mole/liter) was added. The water was removed by blowing air through the mixture, and acid III was extracted from the residue with isopropyl alcohol; the yield of product, with mp 105°C (from petroleum ether), was 0.037 g (74%). Acid III was thermally unstable: Slight decomposition was detected during slow heating, even at 90-95°C.

EXPERIMENTAL

1. H. Deibig, J. Geiger, and M. Sander, Makromol. Chem., 145, 123 (1971).
2. H. Johansson and H. Sebelius, Chem. Ber., 52, 745 (1919).
3. H. K. Hall and A. K. Schneider, J. Am. Chem. Soc., 80, 6409 (1958).
4. E. Blaise and P. Bagard, Ann. Chim., [8], 11, 111 (1907).
5. Swiss Patent No. 268530; Chem. Abstr., 45, 3415 (1951).