

Synthesis of 1,3-Dioxolane Derivatives from β -Chlorolactic Acid and Ketones

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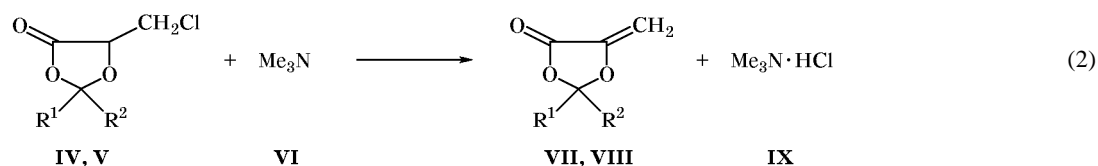
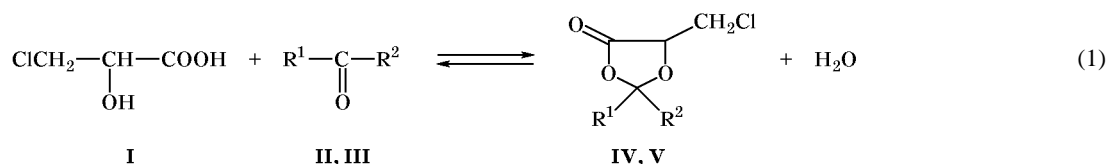
Abstract—2-Ethyl-2-methyl-5-methylene-1,3-dioxolan-4-one and 5-methylene-2,2-pentamethylene-1,3-dioxolan-4-one were synthesized by reaction of β -chlorolactic acid with methyl ethyl ketone and cyclohexanone, respectively, followed by dehydrochlorination of intermediate 5-chloromethyl derivatives.

1,3-Dioxolane derivatives are capable of undergoing polymerization without shrinkage or even with volume expansion. This property allows preparation of UV-cure systems suitable for making optical lenses with a specified gradient of refractive index. Polymerization of 1,3-dioxolane derivatives can involve opening of the dioxolane ring or the cyclic structure can be retained [1]. Compounds having a 1,3-dioxolane ring are usually synthesized on the basis of ethylene glycol, glycerol, epoxy derivatives, and carbonyl compounds [2]. There are almost no published data on the synthesis of 1,3-dioxolanes from β -chlorolactic acid.

In this work we studied the conditions of synthesis of 1,3-dioxolane derivatives from accessible starting compounds, β -chlorolactic acid (**I**) and simplest ketones: methyl ethyl ketone (**II**) and cyclohexanone (**III**). The reactions of **I** with **II** and **III** gave, respectively, 5-chloromethyl-2-ethyl-2-methyl-1,3-dioxolan-4-one (**IV**) and 5-chloromethyl-2,2-pentamethylene-1,3-dioxolan-4-one (**V**). Dehydrochlorination of com-

pounds **IV** and **V** with trimethylamine at 70–75°C resulted in formation of 75% of the corresponding 5-methylene derivatives **VII** and **VIII**.

It is known [3] that reactions like (1) are catalyzed by acids and are reversible. The condensation of β -chlorolactic acid with ketones **II** and **III** was carried out in the presence of 2-acetamido-2-methylpropane-sulfonic acid. Preliminary experiments showed that addition of this catalyst in an amount of 0.1 mol % with respect to acid **I** prevents decomposition of the product during its isolation by neutralization of the reaction mixture. A specific feature of reaction (1) is that ketones **II** and **III** (products of the reverse reaction) form azeotropic mixtures with water (product of the forward reaction) [4]. Therefore, our studies were performed in two lines. According to the first of these, the reagent (ketone) was used as solvent, and experiments of the second series were carried out in an inert solvent, toluene, which also gives an azeotropic mixture with water. In the first series of experiments ketone **II** or **III** was taken in 4–7-fold excess.



II, IV, VII, R¹ = Me, **R**² = Et; **III, V, VIII, R**¹**R**² = (CH₂)₅.

Synthesis of 5-chloromethyl-2,2-pentamethylene-1,3-dioxolan-4-one (**V**) without a solvent (version 1) and with toluene as solvent (version 2); reaction time 2.5 h; 0.1 wt % of catalyst with respect to acid **I**; version 1: molar ratio **III**:**I** 4:1, 100–104°C; version 2: molar ratio **III**:**I** 1.5:1.0, 80°C

Component	Version 1				yield, ^a %	Version 2				yield, ^a %
	charged		isolated			charged		isolated		
	g	mol	g	mol		g	mol	g	mol	
Acid I	36.2	0.29	11.5	0.1	75.3	53.0	0.43	17.3	0.14	99.8
Ketone	116.3	1.16	86.6	0.9		88.0	0.88	59.5	0.59	
Toluene						90.0	1.05	65.6	0.76	
Product V			30.6	0.1				58.8	0.29	
Total		1.45		1.1			2.36		1.78	
Azeotrope in the Dean–Stark trap										
Ketone			18.5							
Water			5.2					5.2		
Toluene								24.7	0.29	
Total		1.45		1.3		2.36		2.07		

^a On the reacted acid **I**.

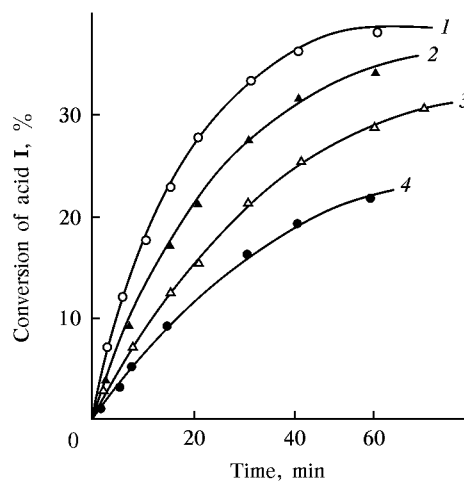
Calculation of the material balance for reaction (1) performed with excess ketone **III** showed that in 2.5 h the amount of water removed as azeotrope from the mixture was equal to stoichiometric (with respect to acid **I**). However, the selectivity of the reaction was 70–75%, presumably due to side processes including condensation of acid **I** and formation of lactide [5]. We succeeded in minimizing the contribution of side processes by carrying out the reaction in toluene. In this case, the boiling point of the azeotrope and hence the reaction temperature changed. Figure shows the kinetic curves plotted for the conversion of acid **I** at various temperatures. These curves reflect the reversible character of reaction (1) and are typical of exothermic processes. The rate constants for transformation of acid **I** and the energy of activation calculated therefrom are consistent with those found previously for the synthesis of dioxolane alcohols from glycerol and ketones. This suggests a common mechanism of these reactions.

Comparison of the results obtained with excess ketone **III** and with toluene as solvent (see table) shows that the second procedure is preferred. It ensures higher selectivity of the process and lower consumption of ketone **III**. It is advisable to perform the reaction with ketone **II** using a 58% aqueous solution of acid **I**. In this case, a triple azeotrope is formed (ketone **II**–water–toluene); the selectivity of the process reaches 93%.

After separation of unreacted acid **I** and catalyst from the toluene solutions, compounds **IV** and **V** were subjected to dehydrochlorination.

EXPERIMENTAL

The progress of reactions was monitored, and the products were identified, by GLC, polarography, and IR spectroscopy. Chromatographic analysis was performed on a Chrom-5 chromatograph using a 3 × 2500-mm glass column packed with 15% PEGA on



Conversion of acid **I** with time at (1) 70°C, (2) 80°C, (3) 90°C, and (4) 100°C; molar ratio ketone **III**–acid **I** 5:1.

Diatom C AW, oven temperature programming mode. *N*-Methylpyrrolidone was used as internal standard in the synthesis of compound **VIII**, and 4-hydroxy-methyl-1,3-dioxolane, in the synthesis of **VII**. Polarographic analysis was performed on an ON-105 instrument with a dropping mercury electrode ($m^{2/3} \times r^{-1/6} = 1.59$) and a saturated calomel electrode as reference. The IR spectra were obtained from samples prepared as thin films using a Jasco A 302 spectrophotometer. The most characteristic absorption bands are as follows: stretching vibrations of the ester groups: 1180 and 1720–1800 cm^{-1} ; stretching vibrations of the C=C bond: 1620–1640 cm^{-1} ; and stretching vibrations of the C–Cl bonds: 600–800 cm^{-1} . Acid **I** was quantitated by acid–base titration with phenolphthalein.

The reactions were carried out in a reactor equipped with a thermometer, a Dean–Stark trap, and a reflux condenser. The mixture was vigorously stirred at a constant temperature. β -Chlorolactic acid (**I**) was obtained by oxidation of epichlorohydrin with HNO_3 at the pilot plant of the Kargin Research Institute of Polymers, following the procedure described in [6]. The catalyst was 2-acetamido-2-methylpropanesulfonic acid which was obtained from acetonitrile, isobutylene, and oleum; the pure and dry catalyst had mp 180°C. The other reagents and solvents conformed to appropriate technical specifications.

5-Chloromethyl-2-ethyl-2-methyl-1,3-dioxolan-4-one (IV). Ketone **II**, 93 g, and toluene, 200 ml, were added to 181 g (0.847 mol) of 58% acid **I**, the mixture was heated to 75°C, and 1.33 g (6.8 mmol) of the catalyst was added. The mixture was heated at 75–80°C with removal of the ketone **II**–water–toluene azeotrope which was collected using a Dean–Stark trap. Ketone **II** was separated from the azeotropic mixture and was used in further syntheses. The reaction mixture was neutralized with 4 equiv of aqueous NaHCO_3 (with respect to the catalyst), sodium 2-acetamido-2-methylpropanesulfonate was filtered off, and the filtrate was distilled under reduced pressure. Yield of **IV** 85%. Colorless liquid, bp 97°C (6 mm), n_D^{20} 1.4502.

5-Chloromethyl-2,2-pentamethylene-1,3-dioxolan-4-one (V) was synthesized under the conditions given in table. The mixture was cooled, neutralized

with 15.2 g of NaHCO_3 , and distilled under reduced pressure. Yield of **V** 80–82%. Red–orange liquid, bp 74°C (1 mm), n_D^{20} 1.4952.

2-Ethyl-2-methyl-5-methylene-1,3-dioxolan-4-one (VII). A mixture of 42.2 g (0.23 mol) of compound **IV**, 250 g (2.47 mol) of amine **VI**, and 0.1 g (0.605 mmol) of 4-*tert*-butyl-1,2-benzenediol (as inhibitor) was stirred for 1.5 h at 70–75°C. The precipitate was filtered off, and the filtrate was distilled under reduced pressure. Yield of **VII** 75–80%. Colorless liquid, bp 75°C (1 mm), n_D^{20} 1.4430.

5-Methylene-2,2-pentamethylene-1,3-dioxolan-4-one (VIII). The mother liquor obtained in the synthesis of compound **V** [it contained 58.75 g (0.286 mol) of compound **V** in toluene] and 0.34 g (2.06 mmol) of the inhibitor were added to 86.29 g of trimethylamine (**VI**). The mixture was heated for 2.5 h at 70–75°C, cooled, neutralized, and distilled under reduced pressure. Yield of **VIII** 90–93%. Colorless liquid, bp 82.5°C (4 mm), n_D^{20} 1.5002.

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