SYNTHESIS OF MEVALONOLACTONE FROM 4-(β-HYDROXYETHYL)-4-METHYL-1,3-DIOXANE

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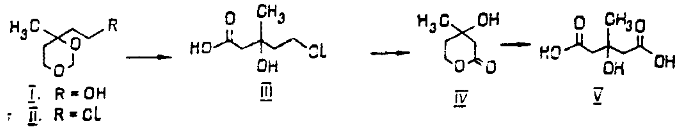
A method has been developed for obtaining mevalonolactone and 3-hydroxy-3-methylglutaric acid from an industrial waste, 4-(β-hydroxyethyl)-4-methyl-1,3-dioxane.

Mevalonolactone is an important biochemical intermediate and, in particular, a growth factor in lactic acid fermentation. A number of synthetic methods of obtaining mevalonolactone have been described in the literature [1-4]. Their main defect is the poor availability of the starting materials.

We have shown that mevalonolactone can be obtained from 4-(β-hydroxyethyl)-4-methyl-1,3-dioxane (HEMD, I) — a multitonnage (5000 tons/year) waste from the manufacture of isoprene by the Prins method [5]. On the interaction of HEMD and thionyl chloride only the hydroxy function is affected, with the formation of 4-(β-chloroethyl)-4-methyl-1,3-dioxane (II). The latter, on reaction with 50% nitric acid at 30-35°C, is converted into 5-chloro-3-hydroxy-3-methylvaleric acid (III). The acid (III) obtained, on interaction with potassium carbonate in the presence of Katamin AB in acetone is converted with a yield of 60% into mevalonolactone (IV). It is interesting to note that under the action of 50% nitric acid mevalonolactone is oxidized, without undergoing dehydration, forming another natural compound, 3-hydroxy-3-glutaric acid (V) [6].



EXPERIMENTAL

PMR spectra were taken on a Perkin—Elmer R-12B instrument with a working frequency of 60 MHz. The analyses of compounds (II) and (III) corresponded to the calculated figures.

4-(β-Chloroethyl)-4-methyl-1,3-dioxane (II). At 20°C, 14.3 g (0.12 mole) of thionyl chloride was added to a mixture of 14.6 g (0.1 mole) of HEMD and 20 ml of pyridine, after which water was added, the product was extracted with ether, and the ethereal extract was dried with magnesium sulfate. This gave 10 g (61%) of compound (II), bp 93-96°C/11 mm, n_D^{20} 1.4611. $C_7H_{13}ClO_2$.

5-Chloro-3-hydroxy-3-methylvaleric Acid (III). At room temperature, 0.1 g of sodium nitrite was added to 56 ml of 50% nitric acid (d 1.31) and then, at 40-45°C, 16.5 g (0.1 mole) of compound (II) was added dropwise and the reaction mixture was stirred at the same temperature for 5 h. The bulk of the nitric acid was distilled off, water (2 × 50 ml) was added to the residue and the water was distilled off from the reaction mixture completely. This gave 14 g (87%) of compound (III), mp 48-50°C (from benzene). $C_6H_{11}ClO_3$. PMR spectrum (in water), δ, ppm: 3.65 t (2H, CH_2Cl), 2.58 s (2H, CH_2), 2.02 t (2H, CH_2CH_2Cl), 1.25 s (3H, CH_3).

Mevalonolactone (IV). At 20-25°C, 6.9 g (0.05 mole) of potassium carbonate was added to a mixture of 8.4 g (0.05 mole) of compound (III), 0.1 g of Katamin AB, and 50 ml dry acetone, and the reaction mixture was heated at 40-45°C for 3 h. After the precipitate had been filtered off, distillation yielded 3.9 g (60%) of mevalonolactone (IV), bp 137-140°C/3 mm, n_D^{20} 1.4740 [4].

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3-Hydroxy-3-methylglutaric Acid (V). At room temperature, 0.1 g of sodium nitrite was added to 20 ml of 50% nitric acid (d 1.31), and this was followed at 35-40°C by 5.2 g (0.04 mole) of mevalonolactone (IV) and the reaction mixture was stirred at the same temperature for 5 h. The bulk of the nitric acid was distilled off, water (2 × 50 ml) was added to the residue, and the water was distilled off from the reaction mixture completely. The residue was dried in the air and, after recrystallization from acetone, 4.8 g (76%) of the acid (V) was obtained with mp 110°C [6].

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STRUCTURE OF PORPHYRINS OF KARAZHANBASS PETROLEUM

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The spectral type and structure of the porphyrins isolated from Karazhanbass petroleum have been studied with the aid of electron spectroscopy in combination with the PMR method.

The wide use of porphyrins and metalloporphyrins as medicinal preparations, semiconductors, and sensitizers and the creation from porphyrins of catalysts for chemical and enzymatic processes, and also the synthesis of expensive derivatives of them, explain the great interest in investigations of petroleum porphyrins [1, 2]. In the present paper we consider the composition and structure of the porphyrins of the Karazhanbass petroleum with high levels of the vanadyl complex (230 mg/100 g of petroleum) and of the nickel complex (23.9 mg/100 g of petroleum) of the porphyrins, which have been studied by the methods of electron spectroscopy, electron spin resonance (ESR), and proton magnetic resonance (PMR).

Metalloporphyrin concentrates were isolated by extraction with acetone. The vanadyl and nickel porphyrins of the Karazhanbass petroleum were separated by the procedure of [3] with the aid of absorption column chromatography on silica gel. The nickel porphyrins were eluted with hexane—benzene (1:1) and the vanadyl porphyrins with chloroform. To identify the nickel and vanadyl porphyrins and to determine their ratio we used the results of their electronic absorption spectra in the visible region (Fig. 1). The total amount of vanadyl complexes was checked by the ESR method [14].

Baker et al. [5] have proposed to use the ratio of intensities α/β of the bands of the nickel complexes (Fig. 1b) to evaluate the relative amount of deoxophylloerythroetioporphyrin (DPEP) and etioporphyrin (EP) in a mixture. In the case of the complex that we are studying, this ratio is 3.0, showing that in petroleum nickel porphyrin is present in the form of the etio type.

It is known that the magnitude α/β can also be used for a preliminary characterization of the composition of vanadyl complexes of geoporphyrins if their spectral types are known; however, as will be shown below, to estimate the comparative amounts of DPEP and EP the use of the ratio α/β for the preliminary characterization of the vanadyl complexes of porphyrins has proved to be unsuitable because of their mutual superposition ($\alpha/\beta = 1.75$) (Fig. 1a).

A more commonly used method of determining spectral types is an analysis of the electronic spectra of the demetallated porphyrins. To prepare them for investigation, a benzene solution of vanadyl porphyrins was subjected to demetallation with concentrated sulphuric acid as in [3]. After purification, the free porphyrins with different structures were separated with the aid of column chromatography on silica gel LS 5/40. Benzene was used as the eluent. The porphyrins of the etio series were eluted first and were followed by the DPEP.

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