## SOME PROPERTIES AND TRANSFORMATIONS OF $\gamma$ -ACETOPROPYL ALCOHOL

E. E. Mikhlina, A. D. Yanina, and L. N. Yakhontov

 $\gamma$ -Acetopropyl alcohol (I) is an intermediate product in the production of a number of important medicinal preparations: vitamin B<sub>1</sub>, quinocide, aminoquinol, trichomonacide, etc. However, the properties of this extremely reactive compound have been studied with insufficient completeness.

UDC 615.31:547.484.43

I was first described in 1889 [1]. In this work and in a number of subsequent studies [2-7] it was indicated that in the case of prolonged boiling in the presence of acids, I is converted both to 2-methyl-4,5-dihydrofuran (II) and to 2-methyl-2-( $\gamma$ -acetopropoxy)-tetrahydrofuran (III). In the first case, evidently the tautomeric cyclic form of  $\gamma$ -acetopropyl alcohol (IV) is dehydrated, and III is formed as a result of the addition of I to the originally formed II:



We found that the conversion of I to the cyclic compounds II and III can occur not only during boiling in the presence of acids, but also under mild conditions without the addition of acids. It was shown that I, produced by alkaline hydrolysis of  $\alpha$ -aceto- $\gamma$ -butyrolactone (V) does not contain II and III directly after redistillation. However, upon standing in the absence of water at room temperature, II and III are gradually formed from I, and the amounts of these substances increase to 7% after 20 days, to 16% after 54 days, and then to 30%.

The content of II and III and I was found according to the difference in the results of the determination of the sum of these three compounds by oxime formation and determination of I by acetylation of the free hydroxy group.

In addition, II and III were isolated from samples of I after prolonged exposure at room temperature: II by fractional redistillation up to 120°, III by vacuum distillation after preliminary treatment with anhydrous potash.

For identification, II and III were produced by countersynthesis. For III, the preparation of which in pure form [4] presented considerable difficulties, we developed a new method of synthesis, consisting of the interaction of II with I without a catalyst or in the presence of catalytic amounts of acetic acid, which permits the production of III in a high yield. II was synthesized according to the well known method of [6].

The observed conversions of I to cyclic compounds II and III under mild conditions are evidently the cause of the presence of substantial amounts of II and III in commercial I. These impurities cannot be removed by fractional distillation, since in the redistillation II and III form azeotropic mixtures with I. Moreover, prolonged heating of I during the process of fractional distillation in turn promotes its conversion to cyclic compounds II and III.

S. Ordzhonikidze All-Union Pharmaceutical Chemistry Scientific-Research Institute, Moscow. Translated from Khimiko-Farmatsevticheskii Zhurnal, Vol. 4, No. 6, pp. 26-28, June, 1970. Original article submitted June 10, 1969.

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As a result of our investigations, we found conditions permitting the conversion of the cyclic compounds II and III to I without their preliminary removal. These investigations were based on the reversibility of the formation of II and III from I. In the presence of a sufficient amount of water, II and III, existing in a mixture with I, add a water molecule and are reconverted to I. We discovered in this case that in the indicated process the deciding factor is the pH of the aqueous solution. At pH 7.0-7.3, the rate of opening of the cyclic compounds II and III is extremely low; the reaction is accelerated in the case of III at pH 5.5. However, under these conditions II is split out only after 40 h of shaking. The reaction proceeds most smoothly in the presence of dilute hydrochloric acid [4, 8-11] (pH 1.5-2.5). These data lay at the basis of the proposed method for improving the quality of commercial I, containing substantial amounts of cyclic compounds II and III.

## EXPERIMENTAL

Conversions of  $\gamma$ -Acetopropyl Alcohol (I). I was produced by hydrolysis of V with an aqueous solution of potash and contained 99% of the basic substance according to acetylation and 98.8% according to oxime formation. After eight months of storage at room temperature, the content of I according to acetylation was lowered to 73.6%.

A. A mixture of 50 g I (73.6% according to acetylation) and 2.5 g calcined potash was mixed periodically for 3 h. The potash was filtered off, and the substance distilled under vacuum. Two basic fractions were collected: 1) bp 102-103° (15 mm), 31.9 g-I- and 2) bp 116-117° (10 mm), 9.3 g-III. Found, %: C 64.16; H 9.55.  $C_{10}H_{18}O_3$ . Calculated, %: C 64.48; H 9.73.

B. I (73.6% according to acetylation) was heated to  $120^{\circ}$ . The distillate with water was collected, dried with potash, and redistilled. We obtained II, bp 79°, IR spectrum coinciding with the IR spectrum of the synthesized sample of II [6].

<u>Production of 2-Methyl-2-( $\gamma$ -acetopropoxy)-tetrahydrofuran (III).</u> A. To a mixture of 20 g II and 24.3 g I (100% according to acetylation) we added 0.1 ml of glacial acetic acid and left it at room temperature for 48 h. Then the reaction mixture was shaken periodically with calcined potash for a period of 2 h, filtered, and redistilled. Yield 39.4 g (89.2%), bp 116-117° (10 mm).

Found, %: C 64.34; H 9.69. C<sub>10</sub>H<sub>18</sub>O<sub>3</sub>. Calculated, %: C 64.48; H 9.73.

B. A mixture of 12.12 g I (98.3% according to acetylation) and 10 g II was kept at room temperature for 20 days, then redistilled under vacuum. Yield 13.4 g (60.6%), bp. 122-123° (13 mm). Found, %: C 64.33; H 10.09.  $C_{10}H_{18}O_3$ . Calculated, %: C 64.48; H 9.73.

Production of  $\gamma$ -Acetopropyl Alcohol without Admixtures of Cyclic Products II and III. A mixture of 50 g commercial I (73.6% according to acetylation) was mixed for 2 h with 30 ml of 0.001 N hydrochloric acid solution at 20-22°, then dried with potash and extracted with chloroform. The chloroform solution was dried with potash, evaporated, and the residue redistilled under vacuum. Yield 45.8 g I (91.5%), content of the basic substance 98.6% both according to acetylation and according to oxime formation.

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