PREPARATION OF γ-ACETOPROPYL ALCOHOL FROM γ-BUTYROLACTONE

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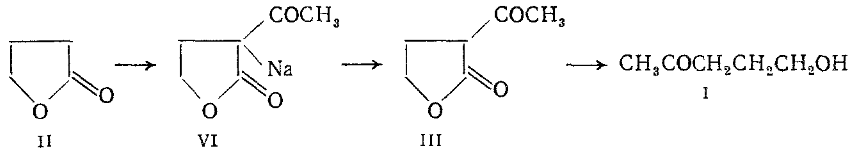
γ-Acetopropyl alcohol (I) is an important intermediate product in the synthesis of vitamin B_1. The known methods for the preparation of (I) γ-butyrolactone (II) [1, 2] include two stages: the condensation of I with alkyl acetate in the presence of metallic sodium or its alcoholate, the hydrolysis and decarboxylation of α-aceto-γ-butyrolactone (III) thus obtained in the potassium carbonate solution.



The method for the preparation of III using metallic sodium as the condensing agent could not be industrially applied because of the danger of explosion in the process, since the condensation reaction proceeds with intense evolution of heat. The drawback of the method is also the use of a water-immiscible solvent (toluene, methylene chloride) for the extraction of III from the reaction mixture, which led to the formation of a four-component mixture during the distillation of solvents, which was difficult to regenerate.

Carrying out of the hydrolysis in a 30% solution of potassium carbonate at 100-110°C led to an abundant precipitation of salts. Separation of crude I (salting out with potassium carbonate) and treatment of the crude fractions of I with potassium carbonate increased considerably the time of the process, and led to a loss of the product.

To eliminate these drawbacks, we investigated the replacement of sodium by a safer condensing agent and improvement in the technology of the preparation of I. We thoroughly studied a method based on the use of sodium ethoxide as the condensing agent. It should be noted that the yield of I and III is very dependent on the quality of ethyl acetate and sodium ethoxide. The entry of moisture and the use of ethyl acetate with a high content of alcohol are not permitted in the condensation. When the content of the alcohol in ethyl acetate was 5%, the yield of III decreased by 2.5%, when it was 10%, by 7%, at a 15% content, by 10%, and at a 50% content of the alcohol, the yield of III decreased by 28%.

The yield at the first stage can be increased (by 6-8%) by increasing the reaction temperature (pressure, use of a high-boiling alkyl acetate); the reaction time can thus be shortened by a factor of 8. We developed a variant using butyl acetate instead of ethyl acetate. The time of reaction was 30 minutes, the temperature 104-106°C. In this case, the extraction of III from reaction mixture can also be carried out with butyl acetate. The drawback of the method is that a four-component mixture of solvents is obtained: butyl acetate (51%)—butanol (37-38%)—ethanol (∿1%)—water (6-7%).

To simplify the regeneration of ethyl acetate, we tried to distill it immediately after the condensation reaction. In this case, the yield of III practically did not change, and the distilled mixture had the following composition: ethyl acetate 65-75%, alcohol 30-35%.

The same purpose (to obtain a two-component system of solvents) can be achieved by isolating the sodium derivative (IV) in a crystalline state, and distilling the solvents from the mother liquors. But this route is less convenient.

At the hydrolysis and decarboxylation state of III, we decreased the amount of potassium carbonate solution by a factor of 1.7-2, and its concentration to 15%, which made it

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TABLE 1. Preparation of Acetopropyl Alcohol (I) under Different Conditions

Condensing agent	Alkyl acetate	Intermediate product	Number of components in mixture of solvents	Potassium carbonate solution		Yield, calculated on II, %	
				ratio to II (by volume)	concentration, %	III	I
Metallic sodium	Ethyl acetate	III distilled	4	0.9:1	30-35	65	49
As above	"	IV crystalline	2	2.5:1	30-35	67	50
Sodium in toluene	"	III crude	3	0.9:1	30-35	66	49
Sodium ethoxide	"	III crude	2	0.9:1	30-35	64	47
"	"	III crude	2	0.5:1	15	64	56
"	Butyl acetate	III crude	4	1:1	30-35	70	55
Potassium isobutoxide in toluene	Ethyl acetate	III distilled	4	—	—	69	—
Sodium ethoxide in toluene	"	III distilled	4	—	—	65	—

Note. 1. In the second line [sic] the yields of IV and I without the treatment of mother liquors are given. 2. The yields of III are given for the distilled product.

possible to eliminate the isolation of crude I (salting out, separation of layers), to shorten the time of the process to 6 h, and to increase the yield of I by 5%.

Data on the yield of I and III for all the variants described are given in Table 1.

Table 1 shows that the highest yield of III (70%) was obtained when butyl acetate was used in the synthesis, and the highest yield of I (56%), when a 15% solution of potassium carbonate and II were used in a ratio of 0.5:1 by volume, and without isolation of crude I.

EXPERIMENTAL

α-Aceto-γ-butyrolactone (III). A 47.5-g portion of dry sodium ethoxide was added to a mixture of 59.2 g of II and 154 ml of ethyl acetate. The temperature may thus increase to 40-50°C. The reaction mixture is heated to 75°C, and kept at this temperature for 3 h, and then cooled to 50°C. The mixture of ethyl acetate and alcohol (120-130 ml) is then distilled under slightly reduced pressure at the temperature of the mixture not exceeding 50-60°C.

A 150 ml portion of water is added to the residue, the mixture is heated to complete dissolution, and cooled to 18°C, and concentrated hydrochloric acid is added slowly to pH 4.8-5.2 at a temperature of the reaction mixture of 18-20°C. The mixture is extracted with methylene chloride. After distillation of methylene chloride from the extract, 85-90 g of crude III are obtained.

γ-Acetopropyl Alcohol (I). A mixture of 85-90 g of crude III and 24 ml of 15% potassium carbonate solution is heated to 104-106°C, while low-boiling solvents are distilled at the same time. The downward sloping condenser is switched over to a reflex condenser, and water is added in an amount equal to the volume of the solvents distilled off. The reaction mixture is then left to stand for 7 h at 104-106°C.

When cool, the mixture is distilled *in vacuo*. The fraction boiling at 100-105°C (10 mm) was collected in an amount of 41 g. This fraction contained 95% of I. Yield 56%, calculated on II.

LITERATURE CITED

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