### CONDITIONS FOR THE ISOMERIZATION OF

### $\alpha$ -ALKYL(OR ARYL)FURFURYL ALCOHOLS

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The cleavage of the furan ring under the action of mineral acids was discovered in 1887 by Dietrich and Paal [1] for the case of 2-methylfuran. This reaction was later studied by various investigators [2], who showed that many furan compounds can undergo this sort of change. In 1932 Chichibabin [3], who carried out the isomerization of  $\alpha$ -alkylfurfuryl alcohols, proposed a mechanism for this reaction. However, a more detailed study of the mechanism was carried out in 1944 by Ushakov and Kucherov [4]. Having isolated and established the structures of the intermediate products in the isomerization, they showed that the transformations of  $\alpha$ -alkyl(or aryl)furfuryl alcohols into  $\gamma$ -keto acids have ionotropic mechanisms associated with the migration of double bonds.

This interpretation of the mechanism later found confirmation in the work of Lewis and others [5].

As we have reported previously [6], for the synthesis of sulfur-containing heterocyclic compounds we prepared a series of  $\alpha$ -alkyl(and aryl)furfuryl alcohols from organomagnesium compounds and 2-furaldehyde, and we carried out their isomerization into the ethyl esters of the corresponding  $\gamma$ -keto acids. In view of the relatively limited data in the literature on the isomerization of  $\alpha$ -alkylfurfuryl alcohols, we turned particular attention on the choice of optimum conditions, under which the yields of isomerization products would attain maximum values. In the isomerization of  $\alpha$ -alkylfurfuryl alcohols of low molecular weight, Ushakov and Kucherov [4] used 0.35-0.5% of hydrogen chloride in alcohol. This concentration was found to be quite inadequate for the isomerization of alcohols of high molecular weight. Thus, in the isomerization of  $\alpha$ -7-methylheptylfurfuryl alcohol with 0.3% alcoholic hydrogen chloride the yield of ethyl 6-methyl-4-oxododecanoate was only 5.5%. If, however, the concentration of HCl was raised to 8.5%, the yield of product was increased to 50%. Chichibabin [3] also used a low concentration of hydrogen chloride, irrespective of the structure of the original alcohol. We found that the concentration of hydrogen chloride and the time for which the reaction mixture is boiled have to be varied according to the molecular weight and structure of the  $\alpha$ -alkylfurfuryl alcohol taken.

$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Original furfuryl alcohol	HC1 concn. (%)	Time of boil ing (hr)	Yield of y- keto ester (%)	Original furfuryl alco- hol	HCl concn. (%)	Time of boil- ing (hr)	Yield of γ- keto ester (%)
$\begin{array}{c} \alpha - \text{ropynulturyl alcohol} & 0.38 & 3 & 46.7 & \alpha - \text{Pentylfurfuryl} & 0.2 & 3 & 6.7 \\ \alpha - \text{Isopropylfurfuryl alcohol} & 0.36 & 3 & 52 & \text{alcohol} & 3.7 & 0.5 & 34.7 \\ \alpha - \text{Butylfurfuryl alcohol} & 0.35 & 3 & 49 & \text{alcohol} & 3.2 & 0.5 & 49.7 \\ \alpha - \text{s-Butylfurfuryl alcohol} & 0.35 & 3 & 64 & \alpha - \text{Octylfurfuryl alcohol} & 5.3 & 0.5 & 47.7 \\ \alpha - \text{Isobutylfurfuryl alcohol} & 0.35 & 3 & 64 & \alpha - \text{Octylfurfuryl alcohol} & 5.3 & 0.5 & 47.7 \\ \alpha - \text{Isobutylfurfuryl alcohol} & 0.35 & 3 & 46 & \text{furyl alcohol} & 8.5 & 0.5 & 50.7 \\ \alpha - \text{Isobutylfurfuryl alcohol} & 0.5 & 52 & \alpha - \text{Decylfurfuryl} & 6.3 & 0.5 & 30 \\ \alpha - t - \text{Butylfurfuryl alcohol} & 0.5 & 3 & 21 & 12.7 & 0.5 & 46 \\ \alpha - \text{Pentylfurfuryl alcohol} & 0.5 & 3 & 38.5 & \alpha - \text{Benzylfurfuryl} & 0.4 & 3 & 17* \\ \alpha - \text{Pentylfurfuryl alcohol} & 0.5 & 3 & 38.5 & \alpha - \text{Benzylfurfuryl} & 0.4 & 3 & 17* \\ \end{array}$	$\alpha$ -Methylfurfuryl alcohol $\alpha$ -Ethylfurfuryl alcohol $\alpha$ -Division alcohol	0,2 0,35	3 3	38 48	α-Isopentylfurfuryl alcohol	0,39	3	44
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	a-riopynunuryi alconol	0,38	3	46,7	α-t-Pentylfurfuryl	0,2	3	6,6
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		0,30	3	52	α-Hentylfurfuryl	3.2	0,5	49.6
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\alpha$ -Butylfurfuryl alcohol	0.35	3	49	alcohol	0,2	0,0	10,0
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	$\alpha$ -s-Butylfurfuryl alcohol	0,35	3	64	α-Octylfurfuryl alcoho	15,3	0,5	47,5
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\alpha$ -Isobutylfurfuryl alcohol	0,3 2,0	$^{3}_{0,5}$	46 52	α-(1-Methylheptyl)fur- furyl alcohol α-Decylfurfuryl alcohol	0,35 8,5 6,3	$ \begin{array}{c} 3 \\ 0,5 \\ 0,5 \\ 0.5 \\ 0.5 \\ \end{array} $	5,5 50,0 30 59,6
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\alpha$ -t-Butylfurfuryl alcohol	0.5	3	21		12.7	0.5	46
$\alpha$ -Pentylfurfuryl alcohol 0.5 3 38.5		4,0	0,5	38	α-Benzylfurfuryl	0,4	3	17*
$4,2$ $0,5$ $48$ $\alpha$ -Phenethylfurfuryl $0,35$ $3$ $47$	$\alpha$ -Pentylfurfuryl alcohol	$0,5 \\ 4,2$	$^{3}_{0,5}$	38,5 48	$\alpha$ -Phenethylfurfuryl	0,35	3	47
alcohol	* As soid				alcohol			

It is known that all  $\alpha$ -alkylfurfuryl alcohols are extremely acidophobic, but they nevertheless differ amongst themselves in stability toward acids. Thus,  $\alpha$ -alkylfurfuryl alcohols of low molecular weight and those containing a tertiary carbon atom in the side chain are strongly resinified in an alcoholic solution of hydrogen chloride, and the yields of isomerization products did not exceed 30-40% in spite of the fact that we used very varied reaction conditions. For the isomerization of alcohols of high molecular weight and normal structure an increased concentration of hydrogen chloride was required: when the concentration of hydrogen chloride was low, part of the starting substance was recovered unchanged. Thus, we found that in the isomerization of  $\alpha$ -decylfurfuryl alcohol in alcoholic solution containing 9.5% of HCl the yield of ethyl 4-oxopentadecanoate attained 60%. If, however, the concentration of hydrogen chloride was reduced to 6%, the yield of isomerization product was lowered to 30%. An excessively high concentration (13%) also lowers the yield (to 46%) because of increased resin formation.

A peculiar isomerization picture was found in the case of the three furfuryl alcohols containing an aromatic group in the side chain. It was found that, as the phenyl group approaches the hydroxy group in the alcohol, the yield of isomerization products diminishes. Thus, we could not obtain an appreciable amount of the keto ester in the isomerization of  $\alpha$ -phenylfurfuryl alcohol. Even when the minimum concentration of hydrogen chloride was used, there was almost complete resinification of the product.  $\alpha$ -Benzylfurfuryl alcohol is capable of isomerization with formation of ethyl 4-oxo-6-phenylhexanoate, though in low yield (20% of the acid), but we did not succeed in obtaining it in a pure state because of contamination with bibenzyl (present in original alcohol) and with a neutral product of unestablished structure formed in the isomerization. Unlike these two alcohols,  $\alpha$ -phenethylfurfuryl alcohol, according to our own results and those of Kucherov [7], can be isomerized in yields of up to 48%, like an ordinary  $\alpha$ -alkylfurfuryl alcohol.

The effect of the concentration of hydrogen chloride and the duration of the boiling on the yield of  $\gamma$ -keto ester obtained in the isomerization of  $\alpha$ -alkylfurfuryl alcohols can be seen from the table.

# EXPERIMENTAL

# Preparation of Some $\alpha$ -Alkylfurfuryl Alcohols

 $\alpha$ -s-Butylfurfuryl Alcohol. A solution of 260 g of 2-furaldehyde in 300 ml of dry ether was added dropwise at -10° to a constantly stirred Grignard reagent prepared from 94 g of magnesium and 460 g of 2-bromobutane in 1200 ml of dry ether. The reaction mixture was then stirred with cooling for 40 minutes, after which it was boiled for 1.5-2 hours. The resulting magnesium complex was poured onto a large amount of ice, the ether layer that separated was decanted, and the mass of benzylfurfuryl alcohol that remained was carefully extracted with ether. The combined ether extract was washed with saturated potassium carbonate solution, then with 40% sodium bisulfite solution, and finally it was dried with fused potassium carbonate. Solvent was distilled off, and the residue was vacuum-distilled twice through a column. This gave 292 g (70% on the 2-furaldehyde taken) of  $\alpha$ -s-butylfurfuryl alcohol; b.p. 80-82° (4 mm); nD<sup>20</sup> 1.4739; d<sub>4</sub><sup>20</sup> 0.9917; Found MR 43.70; Calculated MR 43.79.

 $\alpha$ -Pentylfurfuryl Alcohol. In a similar way, from 605 g of pentyl bromide, 145 g of magnesium, and 335 g of 2-furaldehyde in 2000 ml of dry ether we obtained 498 g (85%) of the alcohol; b.p. 99-101° (3 mm); nD<sup>20</sup> 1.4695; d<sub>4</sub><sup>20</sup> 0.9772; Found MR 48.03; Calculated MR 48.41. Found: C 71.41; 71.24; H 9.50; 9.37%. C<sub>10</sub>H<sub>16</sub>O<sub>2</sub>. Calculated: C 71.39; H 9.53%.

 $\alpha$ -Isopentylfurfuryl Alcohol [8]. This was prepared similarly from 527 g of isopentyl bromide, 105 g of magnesium, and 297 g of 2-furaldehyde in 1600 ml of dry ether in 85% yield; b.p. 94-94.5° (4 mm); nD<sup>20</sup> 1.4695; d<sub>4</sub><sup>20</sup> 0.9745; Found MR 48.41; Calculated MR 48.41.

 $\alpha$ -t-Pentylfurfuryl Alcohol. This was prepared similarly from 176 g of t-pentyl chloride, 60 g of magnesium, and 120 g of 2-furaldehyde in 1200 ml of dry ether in 69% yield. In view of the instability of the resulting furfuryl alcohol, it was not distilled. It was a slightly colored viscous liquid, nD<sup>20</sup> 1.4808.

<u> $\alpha$ -Heptylfurfuryl Alcohol.</u> This was prepared in 88.3% yield from 564 g of heptyl bromide, 110 g of magnesium, and 249 g of 2-furaldehyde in 2200 ml of dry ether by a procedure similar to those given above, but with the difference that the Grignard reagent was prepared with external heating. The furfuryl alcohol obtained by vacuum distillation through a column had: b.p. 105-106° (2 mm); nD<sup>20</sup> 1.4686; d<sub>4</sub><sup>20</sup> 0.9524; Found MR 57.35; Calculated MR 57.64. Found: C 73.50; 73.31; H 10.47; 10.33%. C<sub>12</sub>H<sub>20</sub>O<sub>2</sub>. Calculated: C 73.43; H 10.27%.

 $\alpha$ -Octylfurfuryl Alcohol. In a similar way, from 314 g of octyl bromide, 64 g of magnesium, and 116.4 g of 2-furaldehyde in 1600 ml of dry ether we obtained 225 g (95.5%) of  $\alpha$ -octylfurfuryl alcohol; b.p. 114-115° (3 mm); nD<sup>20</sup> 1.4670; d<sub>4</sub><sup>20</sup> 0.9351; Found MR 62.40; Calculated MR 62.25. Found: C 74.39; H 10.40%. C<sub>13</sub>H<sub>22</sub>O<sub>2</sub>. Calculated: C 74.24; H 10.54%.

 $\frac{\alpha-(1-\text{Methylheptyl})\text{furfuryl Alcohol.}}{\text{for magnesium, and 140 g of 2-furaldehyde in 750 ml of dry ether in 75% yield. In view of its instability to heat, the product was not distilled. Light fractions were vacuum-distilled off, and the product was then found to be a yellowish liquid; nD<sup>20</sup> 1.4660; d_4<sup>20</sup> 0.9233; Found MR 63.08; Calculated MR 62.27.$ 

 $\alpha$ -Decylfurfuryl Alcohol. This was prepared similarly from 160 g of decyl bromide, 21 g of magnesium, and  $\overline{60}$  g of 2-furaldehyde in 230 ml of dry ether in 82% yield. After vacuum distillation [b.p. 139-142° (2 mm)] the product solidified; m.p. 32-33°. Found: C 75.20; H 10.92%.  $C_{15}H_{26}O_2$ . Calculated: C 75.59; H 10.96%.

<u> $\alpha$ -Benzylfurfuryl Alcohol [9]</u>. This was prepared similarly from 260 g of benzyl chloride, 60 g of magnesium, and 175 g of 2-furaldehyde in 820 ml of dry ether in 31.5% yield. The product was a yellowish viscous liquid; b.p. 115-117° (2 mm); nD<sup>20</sup> 1.5559; d<sub>4</sub><sup>20</sup> 1.1279; Found MR 53.65; Calculated MR 54.65. The low yield of the benzylfurfuryl alcohol is to be explained first by the formation of bibenzyl (10 g, m.p. 51-53°) as a byproduct in the Grignard synthesis, and second by the instability of the benzylfurfuryl alcohol to heat [10]. The refractive index of the benzylfurfuryl alcohol varied over a fairly wide range: nD<sup>20</sup> 1.5549-1.5609.

 $\alpha$ -Phenethylfurfuryl Alcohol [11]. This was prepared similarly from 620 g of phenethyl bromide, 82 g of magnesium, and 248 g of 2-furaldehyde in 1650 ml of dry ether in 92% yield (480 g); b.p. 149-152° (3.5 mm); nD<sup>20</sup> 1.5548.

## Preparation of $\gamma$ -Keto Esters

Ethyl 4-Oxohexanoate [3, 4]. A solution of 215 g of  $\alpha$ -methylfurfuryl alcohol [12] [b.p. 76-77° (23 mm); nD<sup>20</sup> 1.4793] in 820 ml of 0.2% alcoholic hydrogen chloride was boiled for three hours in a water bath, after which the solution was distilled down to one-third bulk and the residue was poured into a saturated solution of potassium carbonate. The product was extracted with ether, and the ether extracts were dried over fused potassium carbonate. Solvent was distilled off, and two vacuum distillations of the residue through a 50-cm column gave 116.5 g (38%) of ethyl 4-oxohexanoate, b.p. 76-77° (3 mm) and nD<sup>20</sup> 1.4330, which corresponds to data in the literature.

Ethyl 4-Oxoheptanoate [3]. This was prepared similarly from 317 g of  $\alpha$ -ethylfurfuryl alcohol [12, 13] [b.p. 70-72° (8 mm); nD<sup>20</sup> 1.4744] in 1160 ml of 0.35% alcoholic hydrogen chloride in 48% yield; b.p. 96-98° (4 mm); nD<sup>20</sup> 1.4312; d<sub>4</sub><sup>20</sup> 0.9780; Found MR 45.60; Calculated MR 45.43.

<u>Ethyl 4-Oxooctanoate</u>. In a similar way, by boiling 279 g of  $\alpha$ -propylfurfuryl alcohol [12] [b.p. 103-104° (25 mm); nD<sup>20</sup> 1.4770] in 850 ml of 0.38% alcoholic hydrogen chloride for three hours we obtained 173 g (46.7%) of ethyl 4-oxooctanoate; b.p. 93-94° (2.5 mm); nD<sup>20</sup> 1.4340; d<sub>4</sub><sup>20</sup> 0.9640; Found MR 50.31; Calculated MR 50.05.

Ethyl 6-Methyl-4-oxoheptanoate [4]. Similarly, from 235 g of  $\alpha$ -isopropylfurfuryl alcohol [12] [b.p. 74-75° (11 mm); nD<sup>20</sup> 1.4725] in 850 ml of 0.35% alcoholic hydrogen chloride we obtained 159 g (52%) of ethyl 6-methyl-4-oxoheptanoate; b.p. 80-81° (3 mm); nD<sup>20</sup> 1.4293; d<sub>4</sub><sup>20</sup> 0.9585; Found MR 50.11; Calculated MR 49.93; Calculated 52%.

Ethyl 4-Oxononanoate [7]. From 336 g of  $\alpha$ -butylfurfuryl alcohol [12, 13] [b.p. 98-100° (5 mm); nD<sup>18</sup> 1.4728] in 1200 ml of 0.35% alcoholic hydrogen chloride we obtained 213 g (49%) of the keto ester, b.p. 111-113° (5 mm) and nD<sup>20</sup> 1.4367, which corresponds to data in the literature.

Ethyl 6-Methyl-4-oxooctanoate. In a similar way, by boiling 292 g of  $\alpha$ -s-butylfurfuryl alcohol in 1100 mł of 0.35% alcoholic hydrogen chloride for three hours we obtained 250 g (64%) of the corresponding  $\gamma$ -keto ester; b.p. 110-111° (4 mm); nD<sup>20</sup> 1.4342; d<sub>4</sub><sup>20</sup> 0.9546; Found MR 54.61; Calculated MR 54.66. Found: C 65.87; 65.64; H 10.18; 10.40%. C<sub>11</sub>H<sub>20</sub>O<sub>3</sub>. Calculated: C 65.96; H 10.06%.

Ethyl 7-Methyl-4-oxooctanoate [7]. This was prepared similarly from 425 g of  $\alpha$ -isobutylfurfuryl alcohol [12] [b.p. 79-80° (4 mm); nD<sup>20</sup> 1.4685] in 1500 ml of 2% alcoholic hydrogen chloride in 52% yield; b.p. 90-91° (3 mm) and nD<sup>20</sup> 1.4330, which corresponds to data in the literature.

Ethyl 6,6-Dimethyl-4-oxoheptanoate [4]. A solution of 179 g of  $\alpha$ -t-butylfurfuryl alcohol [4] (because of its instability to heat the alcohol was not distilled; nD<sup>20</sup> 1.4807) in 570 ml of 4% alcoholic hydrogen chloride was boiled for 30 minutes. The usual treatment and two distillations gave ethyl 6,6-dimethyl-4-oxoheptanoate in 38% yield; b.p. 88-89° (3.5 mm); nD<sup>20</sup> 1.4346; d<sub>4</sub><sup>20</sup> 0.9523; Found MR 54.83; Calculated MR 54.66.

Ethyl 4-Oxodecanoate.  $\alpha$ -Pentylfurfuryl alcohol (190 g) was dissolved in 450 g of absolute alcohol and saturated with 20 g (determined by increase in weight) of dry hydrogen chloride. The reaction mixture was then boiled for 30 minutes and treated as described above. Two distillations gave 116 g (48%) of the  $\gamma$ -keto ester; b.p. 115-116° (3 mm); nD<sup>20</sup> 1.4370; d<sub>4</sub><sup>20</sup> 0.9440; Found MR 59.55; Calculated MR 59.28. Found: C 67.34; 67.23; H 10.30; 10.45%. C<sub>12</sub>H<sub>22</sub>O<sub>3</sub>. Calculated: C 67.26; H 10.35%.

Ethyl 8-Methyl-4-oxononanoate. By boiling 250 g of  $\alpha$ -isopentylfurfuryl alcohol in 900 ml of 0.39% alcoholic hydrogen chloride for three hours we obtained 140 g (44%) of ethyl 8-methyl-4-oxononanoate; b.p. 112-114° (3 mm); nD<sup>20</sup> 1.4373; d<sub>4</sub><sup>20</sup> 0.9432; Found MR 59.55; Calculated MR 59.28. Found: C 67.67; 67.65; H 10.37; 10.58%. C<sub>12</sub>H<sub>22</sub>O<sub>3</sub>. Calculated: C 67.26; H 10.35%.

Ethyl 6,6-Dimethyl-4-oxooctanoate. By boiling 145 g of  $\alpha$ -t-pentylfurfuryl alcohol in 300 ml of 3.7% alcoholic hydrogen chloride for 30 minutes and suitable treatment we obtained 64 g (34.7%) of the  $\gamma$ -keto ester; b.p. 95-97° (2 mm); nD<sup>20</sup> 1.4410; d<sub>4</sub><sup>20</sup> 0.9562; Found MR 59.19; Calculated MR 59.28. Found: C 67.44; H 10.35%. C<sub>12</sub>H<sub>22</sub>O<sub>3</sub>. Calculated: C 67.29; H 10.35%.

Ethyl 4-Oxododecanoate. In a similar way, from 316 g of  $\alpha$ -heptylfurfuryl alcohol in 700 ml of 3.2% alcoholic hydrogen chloride we obtained 194 g (49.6%) of the keto ester; b.p. 131-133° (2 mm); nD<sup>20</sup> 1.4403; d<sub>4</sub><sup>20</sup> 0.9317; Found MR 68.59; Calculated MR 68.52. Found: C 69.47; 69.72; H 10.93; 10.94%. C<sub>14</sub>H<sub>26</sub>O<sub>3</sub>. Calculated: C 69.38; H 10.83%.

Ethyl 4-Oxotridecanoate. This was prepared similarly from 126 g of  $\alpha$ -octylfurfuryl alcohol in 400 ml \*of 5.3% alcoholic hydrogen chloride in 47.5% yield (73 g); b.p. 145-146° (3 mm); nD<sup>20</sup> 1.4430; d<sub>4</sub><sup>20</sup> 0.9256; Found MR 73.43; Calculated MR 73.14. Found: C 70.49; 70.69; H 11.24; 11.16%. C<sub>15</sub>H<sub>18</sub>O<sub>3</sub>. Calculated: C 70.29; H 11.01%.

Ethyl 6-Methyl-4-oxododecanoate. Similarly, by boiling 200 g of  $\alpha$ -(1-methylheptyl)furfuryl alcohol in 600 ml of 8.5% alcoholic hydrogen chloride for 30 minutes we obtained 122 g (50%) of the keto ester; b.p. 123-125° (1 mm). nD<sup>20</sup> 1.4411; d<sub>4</sub><sup>20</sup> 0.9232; Found MR 73.23; Calculated MR 73.135. Found: C 69.98; 69.99; H 10.95; 10.90%. C<sub>15</sub>H<sub>28</sub>O<sub>3</sub>. Calculated: C 70.29; H 11.01%.

Ethyl 4-Oxopentadecanoate. Similarly, from 50 g of  $\alpha$ -decylfurfuryl alcohol in 120 ml of 9.5% alcoholic hydrogen chloride we obtained the keto ester in 59.6% yield. Ethyl 4-oxopentadecanoate is a white crystalline substance, m.p. 25-27° (it crystallizes after two distillations); b.p. 166-167° (2.5 mm). Found: C 72.15; 71.94; H 11.52; 11.58%. C<sub>17</sub>H<sub>32</sub>O<sub>3</sub>. Calculated: C 71.78; H 11.34%.

4-Oxo-6-phenylhexanoic Acid. A solution of 59 g of  $\alpha$ -benzylfurfuryl alcohol in 200 ml of 0.4% alcoholic hydrogen chloride was boiled for three hours in a water bath. After the usual treatment and two distillations we obtained 38.4 g of product, b.p. 127-129° (1.5 mm), nD<sup>20</sup> 1.4898; d<sub>4</sub><sup>20</sup> 1.0311, which was hydrolyzed at the boil for two hours with a solution of 27 g of potassium hydroxide in 250 ml of methanol. The residue remaining after removal of solvent was poured into water, and the upper layer of unhydrolyzed material was extracted with ether; the extract was dried with potassium carbonate and vacuum-distilled: b.p. 140-141 (1 mm); nD<sup>20</sup> 1.4826; d<sub>4</sub><sup>20</sup> 1.0194. Found: C 71.09; 71.13. H 9.22. 9.40%.

The aqueous solution was acidified with concentrated hydrochloric acid, and the yellow precipitate formed was filtered off and crystallized from hot water. We obtained 6 g of 4-oxo-6-phenylhexanoic acid, m.p. 93-94°. Found° C 69.69. 69.73; H 6.72; 6.42%.  $C_{12}H_{14}O_3$ . Calculated: C 69.92; H 6.72%.

Ethyl 4-Oxo-7-phenylheptanoate [7]. Similarly, by boiling 280 g of  $\alpha$ -phenethylfurfuryl alcohol in 1000 ml of 0.35% alcoholic hydrogen chloride for three hours we obtained 162 g (47%) of the keto ester, b.p. 166-169° (3 mm) and nD<sup>20</sup> 1.5010, which corresponds to data in the literature.

#### SUMMARY

1. A study was made of the conditions required for the isomerization of some  $\alpha$ -alkyl(and aryl)furfuryl alcohols in an alcoholic solution of hydrogen chloride.

2. The yield of isomerization product depends considerably on the structure of the  $\alpha$ -alkylfurfuryl alcohol and also on the concentration of hydrogen chloride.

3. Seventeen  $\alpha$ -alkyl(and aryl)furfuryl alcohols and seventeen ethyl esters of  $\gamma$ -keto acids, most of which have not been described previously, were prepared and characterized.

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<sup>\*</sup>Original Russian pagination. See C. B. translation.