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Abstract

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SYNTHESIS AND ISOMERIZATION OF ENOL ACETATES OF β-FURANIDONES

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Derivatives of the enolic form of tetrahydrofuran-3-one (β-furanidone) and its homologs have scarcely been studied at all, and only Dupont [1] mentions that 2,2,5,5-tetramethylfuranidone-3 gives the sulfate of the enolic form (under the action of sulfuric acid) and the sodium derivative of the enolic form (under the action of metallic sodium), which, upon treatment with ethyl bromide, forms 3-ethoxy-2,2,5,5-tetramethyldihydrofuran.

In the present work, to obtain acetyl derivatives of the enolic form, we used ketones of the β-furanidone series in which, in the α-position to the carbonyl group, there is only one methylene group; this makes it possible to obtain only one enol acetate with a predetermined position of the double bond. Isopropenyl acetate [2] was used as the acetylating agent. We found that in this case acetates of the enolic form of ketones of the β-furanidone series are formed in 65–85% yield, calculated on the ketone used in the reaction (acylation with acetic anhydride does not give a positive result). In this way we obtained the enol acetates of: 2,2,5,5-tetramethylfuranidone-3 (75.5%), 2,5-dimethyl-2,5-diethylfuranidone-3 (66%), 2,2,5,5-bistetramethylenefuranidone-3 (80%), and 2,2,5,5-bispentamethylenefuranidone-3 (84.5%).

[structural formula] $+ CH_2 = C(CH_3)OCOCH_3 \longrightarrow$ [structural formula] $+ CH_3COCH_3$

1) $R = R' = CH_3$;

2) $R = CH_3$, $R' = C_2H_5$;

3) [structural formula with R, R' and a cyclobutene fragment]

4) [structural formula with R, R' and a cyclohexene fragment]

This type of interesting derivative of β-furanidones had not previously been described in the literature. It should be noted that in 1940 Yu. S. Zal' kind and V. I. Baranov [3], studying the addition of acetic acid to tetramethylbutynediol

in the presence of mercury salts and relying only on analytical data, erroneously assigned to one of the reaction products (m.p. 30.5-31°, b.p. 88-96°/6.5 mm) the structure of the enol acetate of 2,2,5,5-tetramethylfuranidone-3.

We also studied the behavior of the enol acetates we obtained toward halogenation and isomerization. It turned out that when chlorine is passed at −5° into the enol acetate of 2,2,5,5-tetramethylfuranidone-3 or its solution in chloroform or abs. ether in 67% yield gives an α-monochloroketone of the furanidone series—4-chloro-2,2,5,5-tetramethylfuranidone-3, the formation of which may be explained by the following scheme:

[enol acetate structure] $\xrightarrow{Cl_2}$ [[dichloro acetate intermediate structure]] $\longrightarrow$ [4-chloro-2,2,5,5-tetramethylfura

This reaction is of fundamental, but not preparative, significance, since α-chloroketones of the furanidone series are obtained in good yield by direct chlorination of the corresponding ketones ([4]).

One of the most interesting reactions of ketone enol acetates is their isomerization (thermal or catalytic) into β-diketones. Thus, for example, isopropenyl acetate, under the action of boron trifluoride or when passed through a quartz tube at 450—500°, isomerizes to acetylacetone in 70—83% yield ([5]).

We found that when boron trifluoride is passed into cooled enol acetate of 2,2,5,5-tetramethylfuranidone-3 at −40—−20°, isomerization does not occur, while at −10—−5°, after a certain induction period, a vigorous reaction takes place and the reaction mixture becomes completely resinified.

When the enol acetate of 2,2,5,5-tetramethylfuranidone-3 is passed through a quartz tube packed with glass wool and heated to 500°, isomerization occurs to 4-acetyl-2,2,5,5-tetramethylfuranidone-3 (yield 36.5%). This thermal isomerization occurs within a very narrow temperature interval and with a definite and very short duration of thermal action. At lower temperatures (450—480°) isomerization does not occur; at higher temperatures (510—520°) the yield of 4-acetyl-2,2,5,5-tetramethylfuranidone decreases to 5—10%, owing to its cleavage into a ketone and ketene:

[enol acetate structure] $\xrightarrow{500^\circ}$ [4-acetyl-2,2,5,5-tetramethylfuranidone-3 structure] $\xrightarrow{>500^\circ}$ [2,2,5,5-tetramethyl

The preparation of the copper salt and derivatives of 4-acetyl-2,2,5,5-tetramethylfuranidone-3, as well as its intense violet coloration with a solution of ferric chloride, confirms its structure. The absorption spectrum of the copper salt of 4-acetyl-2,2,5,5-tetramethylfuranidone-3 (λ_{max} 256; 305 mμ) is analogous to the absorption spectrum of the copper salt of acetylacetone (λ_{max} 240; 294 mμ)—a most characteristic β-diketone.

The study of the properties of this class of β-diketones of the furanidone series is continuing.

Experimental Part

Enol acetate of 2,2,5,5-tetramethylfuranidone-3. A mixture of 20 g of isopropenyl acetate, 28.4 g of 2,2,5,5-tetramethylfuranidone-3 ([1]) and 1.5 g of *p*-toluenesulfonic acid was heated in a flask with a 50-cm-high dephlegmator and a descending condenser until 12.5 ml of acetone (86%) had distilled off. After cooling, the mixture was saturated with anhydrous sodium acetate, allowed to stand for several hours, then filtered, and the precipitate was washed with abs. ether. After distilling ether from the combined filtrates and twice distilling the residue, 9.7 g of unchanged ketone and 18.3 g of enol acetate of 2,2,5,5-tetramethylfuranidone-3 were isolated (50% based on the introduced

and 75.5% based on the ketone that entered into the reaction): b.p. 77–78° (19 mm); n_D^{20} 1.4313; d_4^{20} 0.9858; MR_D 48.40; $C_{10}H_{16}O_3$. Calculated: MR_D 49.01; EM_D 0.61.

Found %:	C 65.10; 64.94; H 8.85; 8.79
$C_{10}H_{16}O_3$. Calculated %:	C 65.13; H 8.75

Enol acetate of 2,5-dimethyl-2,4-diethylfuranidone-3 was obtained, as described above, from 17 g of 2,5-dimethyl-2,5-diethylfuranidone-3 ([1]), 20 g of isopropenyl acetate, and 1.5 g of *p*-toluenesulfonic acid; b.p. 105–107° (19 mm); n_D^{20} 1.4441; d_4^{20} 0.9634; MR_D 58.54; $C_{12}H_{20}O_3$. Calculated: MR_D 58.25; EM_D 0.29.

Found %:	C 68.39; 68.26; H 9.61; 9.73
$C_{12}H_{20}O_3$. Calculated %:	C 67.89; H 9.50

Yield 9.7 g (45.5% based on the amount introduced and 66% based on the ketone that entered into the reaction).

Enol acetate of 2,2,5,5-bistetramethylenefuranidone-3 was obtained, as described above, from 19.4 g of 2,2,5,5-bistetramethylenefuranidone-3 ([6]), 20 g of isopropenyl acetate, and 10 drops of concentrated sulfuric acid: b.p. 124–127° (9 mm); m.p. 49° (from alcohol);

Found %:	C 71.14; 71.22; H 8.93; 8.98
$C_{14}H_{20}O_3$. Calculated %:	C 71.16; H 8.53

Yield 9.8 g (41.5% based on the amount introduced and 80% based on the ketone that entered into the reaction).

Enol acetate of 2,2,5,5-bispentamethylenefuranidone-3 was obtained, as described above, from 22.2 g of 2,2,5,5-bispentamethylenefuranidone-3 ([6]), 20 g of isopropenyl acetate, and 10 drops of concentrated sulfuric acid: m.p. 54–55° (from alcohol).

Found %:	C 72.69; 72.87; H 9.30; 9.20
$C_{16}H_{24}O_3$. Calculated %:	C 72.69; H 9.15

Yield 11 g (41.7% based on the amount introduced and 84.5% based on the ketone that entered into the reaction).

Chlorination of enol acetate of 2,2,5,5-tetramethylfuranidone-3. Into 11.5 g of enol acetate of 2,2,5,5-tetramethylfuranidone-3, cooled to −5°, a stream of dry chlorine was passed until a weight increase of 4.4 g was reached. Then the reaction mass, vigorously evolving hydrogen chloride in air, was distilled in a stream of nitrogen under vacuum; 7.3 g (67%) of 4-chloro-2,2,5,5-tetramethylfuranidone-3 was isolated: b.p. 65–66° (8 mm); n_D^{20} 1.4470; d_4^{20} 1.0820; MR_D 43.61; $C_8H_{13}O_2Cl$. Calculated MR_D 43.83; EM_D 0.22.

Found %:	Cl 20.23; 20.17
$C_8H_{13}O_2Cl$. Calculated %:	Cl 20.07

Literature data: b.p. 184.5° (760 mm); n_D^{18} 1.447; d^{18} 1.0925 ([4]). Similar results were obtained in chlorination in chloroform and absolute ether media.

Preparation of 4-acetyl-2,2,5,5-tetramethylfuranidone-3. 14.5 g of enol acetate of 2,2,5,5-tetramethylfuranidone-3 was passed at a rate of 3.75 ml/h through a quartz tube filled with glass wool (inner diameter 10 mm, length of the heated section 100 mm) and heated to 500°. On distillation of the isomerization product under vacuum, 7.2 g of unchanged enol acetate was isolated. Upon addition to the residue, in an amount of 20 ml, of a saturated solution of copper acetate, 3.1 g (36.6%) of the copper salt of 4-acetyl-2,2,5,5-tetramethylfuranidone-3 was obtained; m.p. 285° (from alcohol).

Found %:	C 55.52; 55.37; H 7.11; 7.19
$C_{20}H_{30}O_6Cu$. Calculated %:	C 55.86; H 7.03

On decomposition of 3.1 g of the copper salt of 4-acetyl-2,2,5,5-tetramethylfuranidone-3 with 20% sulfuric acid, 2.5 g (94%) of 4-acetyl-2,2,5,5-tetramethylfuranidone-3 was obtained; m.p. 53° (from absolute alcohol). On standing in air it rapidly converts into a hydrate with m.p. 73°.

Found, %: C 59.57; 59.62; H 9.08; 9.10
$C_{10}H_{16}O_3 \cdot H_2O$. Calculated, %: C 59.38; H 8.97

Semicarbazone: m.p. 156–157° (from cyclohexane).

Found, %: C 54.72; 54.98; H 7.96; 8.17
$C_{11}H_{19}O_3N_3$. Calculated, %: C 54.76; H 7.93

Phenylhydrazone: m.p. 151° (from alcohol).

Found, %: C 70.49; 69.78; H 8.29; 8.12; N 10.15; 10.36
$C_{16}H_{22}O_2N_2$. Calculated, %: C 70.04; H 8.08; N 10.21

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Note: Figure translations are in progress. See original paper for figures.