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> SHORT COMMUNICATIONS

## Synthesis of New 2-Substituted 2,5-Dihydrofuranone Derivatives and Their Chemical Transformations

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2,5-Dihydrofuran-2-ones having functional substituents in the 3-position constitute structural fragments of many natural and synthetic biologically active compounds [1–5]. One of the most general and convenient methods of synthesis of functionally substituted furan-2(5*H*)-ones is based on reactions of  $\alpha$ -hydroxy ketones with compounds containing an activated methylene group [6–8].

In continuation of our studies in this field, in the present communication we report on the synthesis and chemical transformations of a new class of compounds, 2,5-dihydrofuran-2-imines based on readily accessible  $\alpha$ -hydroxy ketones. We found that, contrary to published data [9], tertiary  $\alpha$ -hydroxy ketones react with malononitrile to give mixtures of the corresponding 2,5-dihydrofuran-2-imines I and products of their subsequent reaction with the second malononitrile molecule, 2-(2,5-dihydrofuran-2-ylidene)malononitriles II, which were formed in good yields. Detailed examination of this reaction with a view to find optimal conditions showed that the process occurs even in the absence of a catalyst upon mixing of the reactants in alcohol or benzene.





General procedures for the reactions of  $\alpha$ -hydroxy ketones with malononitrile. *a*. The corresponding  $\alpha$ -hydroxy ketone and malononitrile, 50 mmol each, were added to a solution of 0.115 g (5 mmol) of metallic sodium in 25 ml of anhydrous ethanol. The mixture was kept for 15–20 h at room temperature, the solvent was distilled off under reduced pressure, the residue was dissolved in benzene, and the precipitate was filtered off and recrystallized from ethanol–water (2:1) to isolate compound **Ha** or **Hb**. The benzene solution was diluted with four volumes of hexane, and the precipitate was filtered off and recrystallized from heptane. We thus isolated compound **Ia** or **Ib**.

*b*. A mixture of 50 mmol of  $\alpha$ -hydroxy ketone and 50 mmol of malononitrile in 25 ml of anhydrous ethanol was kept for 15–20 h at room temperature. The mixture was then treated as described above in *a*.

c. A mixture of 50 mmol of  $\alpha$ -hydroxy ketone and 50 mmol of malononitrile in 25 ml of anhydrous benzene was kept for 15–20 h at room temperature. The solvent was partially distilled off under reduced pressure, and the mixture was then treated as described above in *a*.

**2-Imino-4,5,5-trimethyl-2,5-dihydrofuran-3-carbonitrile (Ia).** Yield 43 (*a*), 25 (*b*), 55% (*c*); mp 97– 98°C (oily substance [10]). IR spectrum, v, cm<sup>-1</sup>: 2230 (CN), 1665 (C=N), 1075 (C–O–C), 985 (CH), 890 (CH). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 1.4 s (6H, CH<sub>3</sub>), 2.20 s (3H, CH<sub>3</sub>), 6.45 s (1H, NH). Found, %: C 64.01; H 6.48; N 19.01. C<sub>8</sub>H<sub>10</sub>N<sub>2</sub>O. Calculated, %: C 63.98; H 6.71; N 18.65.

**2-Imino-4-methyl-5,5-pentamethylene-2,5-dihydrofuran-3-carbonitrile (Ib).** Yield 38 (*a*), 17 (*b*), 60% (*c*); mp 89–90°C. IR spectrum, v, cm<sup>-1</sup>: 2225 (CN), 1660 (C=N), 1075 (C–O–C), 980 (CH), 885 (CH). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 1.30–1.40 m (2H, CH<sub>2</sub>), 1.45–1.68 m (8H, CH<sub>2</sub>), 2.40 s (3H, CH<sub>3</sub>), 6.50 s (1H, NH). Found, %: C 69.51; H 7.41; N 14.42. C<sub>11</sub>H<sub>14</sub>N<sub>2</sub>O. Calculated, %: C 69.45; H 7.42; N 14.72.

**2-Dicyanomethylidene-4,5,5-trimethyl-2,5-dihydrofuran-3-carbonitrile (IIa).** Yield 30 (*a*), 65 (*b*), 40% (*c*); mp 202–203°C; published data [10]: mp 196– 198°C. IR spectrum, v, cm<sup>-1</sup>: 3084, 3056, 2992, 2230 (CN), 1620, 1580, 1560, 1435, 1390, 1345, 1210, 1105, 992, 780. <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 1.79 s (6H, CH<sub>3</sub>), 2.35 s (3H, CH<sub>3</sub>). Found, %: C 66.9; H 4.56; N 21.18. C<sub>11</sub>H<sub>9</sub>N<sub>3</sub>O. Calculated, %: C 66.32; H 4.55; N 21.09.

**2-Dicyanomethylidene-4-methyl-5,5-pentamethylene-2,5-dihydrofuran-3-carbonitrile (IIb).** Yield 36 (*a*), 70 (*b*), 20% (*c*); mp 214–215°C. IR spectrum, v, cm<sup>-1</sup>: 3095, 3050, 2990, 2230 (CN), 1625, 1580, 1560, 1440, 1354, 1340, 1205, 1100, 985, 780. <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 1.20–1.30 m (2H, CH<sub>2</sub>), 1.38–1.42 m (2H, CH<sub>2</sub>), 1.65–1.75 m (6H, CH<sub>2</sub>), 2.35 s (3H, CH<sub>3</sub>). Found, %: C 70.67; H 5.31; N 17.72. C<sub>14</sub>H<sub>13</sub>N<sub>3</sub>O. Calculated, %: C 70.28; H 5.48; N 17.56.

The IR spectra were recorded on a Specord 75IR spectrophotometer from samples dispersed in mineral

oil. The <sup>1</sup>H NMR spectra were measured on a Varian Mercury-300 instrument at 300 MHz using hexamethyldisiloxane as internal reference.

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