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SYNTHESIS OF 3-ARYL-4,4-DIMETHYL-2-OXASPIRO[5,5]UNDECANE-1,5-DIONES BY THE REFORMATSKY REACTION

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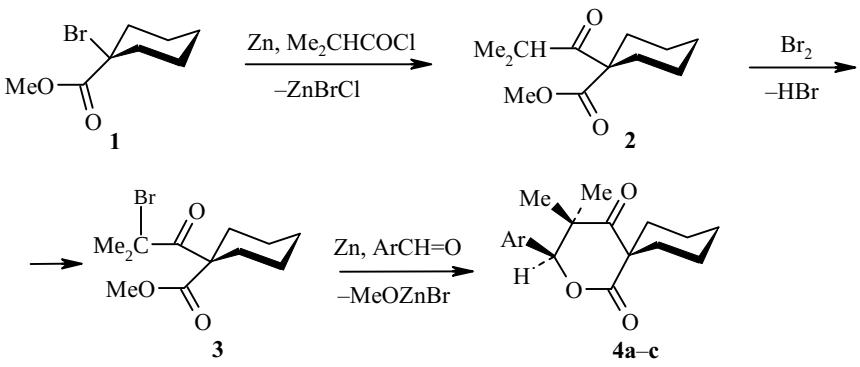
Keywords: 3-aryl-4,4-dimethyl-2-oxaspiro[5,5]undecane-1,5-diones, 1-(2-bromoisobutyryl)cyclohexanecarboxylic acid methyl ester, Reformatsky reaction.

Methods have been described for obtaining substituted 2,3,5,6-tetrahydropyran-2,4-diones [1-4] but there is no information on the synthesis of analogs having a spirocarbon atom at position 3 of the pyran ring. We have developed a method for obtaining such compounds, namely, 3-aryl-4,4-dimethyl-2-oxaspiro[5,5]undecane-1,5-diones (**4a-c**) using the Reformatsky reaction.



4 **a** R = Ph, **b** R = 4-FC_6H_4, **c** R = 3,4-$(MeO)_2C_6H_3$

Keto ester **2** was initially obtained from bromo ester **1**, zinc, and isobutyryl chloride. Product **2** was brominated to give 1-(2-bromoisobutyryl)cyclohexanecarboxylic acid methyl ester (**3**), which reacted with zinc and aromatic aldehydes in 1:3 ether–ethyl acetate to give the desired products **4a-c**.

4,4-Dimethyl-2-oxa-3-phenylspiro[5,5]undecane-1,5-dione (4a). Yield 78%; mp 124-125°C. IR spectrum, cm^{-1}: 1715, 1745. ^1H NMR spectrum (DMSO-d_6, 300 MHz), δ, ppm: 0.87 (3H, s, CH_3); 0.93 (3H, s, CH_3); 1.32-2.22 (10H, m, $(CH_2)_5$); 5.75 (1H, s, –CH–O); 7.37 (5H, s, C_6H_5). Found, %: C 75.32; H 7.65. $C_{18}H_{22}O_3$. Calculated, %: C 75.50; H 7.74.

3-(4-Fluorophenyl)-4,4-dimethyl-2-oxaspiro[5,5]undecane-1,5-dione (4b). Yield 68%; mp 130-131°C. IR spectrum, cm^{-1}: 1730, 1750. ^1H NMR spectrum (DMSO-d_6, 300 MHz), δ, ppm: 0.96 (6H, s, CH_3); 1.30-2.23 (10H, m, $(CH_2)_5$); 5.97 (1H, s, –CH–O); 7.2-7.35, 7.42-7.59 (4H, m, C_6H_4). Found, %: C 71.15; H 6.92. $C_{18}H_{21}FO_3$. Calculated, %: C 71.03; H 6.95.

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3-(3,4-Dimethoxyphenyl)-4,4-dimethyl-2-oxaspiro[5,5]undecane-1,5-dione (4c). Yield 60%; mp 115-116°C. IR spectrum, cm^{-1}: 1720, 1755. ^1H NMR spectrum (DMSO-d_6, 300 MHz), δ, ppm: 0.91 (3H, s, CH_3); 0.93 (3H, s, CH_3); 1.30-2.22 (10H, m, $(CH_2)_5$); 3.77 (3H, s, CH_3O); 3.79 (3H, s, CH_3O); 5.72 (1H, s, –CH–O); 6.92 (1H, d, 5-H_{Ph}); 6.95 (1H, s, 2-H_{Ph}); 6.97 (1H, d, 6-H_{Ph}). Found, %: C 69.26; H 7.49. $C_{20}H_{26}O_5$. Calculated, %: C 69.34; H 7.57.

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