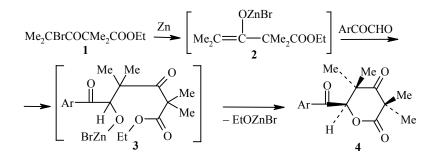
SYNTHESIS OF 6-AROYL-3,3,5,5-TETRAMETHYL-2,3,5,6-TETRAHYDROPYRAN-2,4-DIONES BY THE REFORMATSKY REACTION

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Keywords: aroylglyoxal, 6-aroyl-3,3,5,5-tetramethyl-2,3,5,6-tetrahydropyran-2,4-diones, ethyl ester of 4-bromo-2,2,4-trimethyl-2-oxopentanoic acid, zinc, Reformatsky reaction.

No data are available in the literature on substituted 2,3,5,6-tetrahydropyran-2,4-diones containing an acyl group in the 6 position of the pyran ring [1]. The first representatives of this type of compounds, 6-aroyl-3,3,5,5-tetramethyl-2,3,5,6-tetrahydropyran-2,4-diones, were obtained by the Reformatsky reaction according to the scheme:



4 a Ar = Ph, b Ar = 4-MeC₆H₄, c Ar = 4-ClC₆H₄

In the first step, from the ethyl ester of 4-bromo-2,2,4-trimethyl-3-oxopentanoic acid (1) and zinc (ether-ethylacetate, 3:1), we obtain the zinc enolate 2, which then was reacted with arylglyoxals. As a result of selective reaction of reagent 2 with the aldehyde group of the arylglyoxal, initially the alcoholate 3 was formed, which spontaneously underwent ring closure, yielding the target products 4a-c.

6-Benzoyl-3,3,5,5-tetramethyl-2,3,5,6-tetrahydropyran-2,4-dione (4a). Yield 80%; mp 92-93°C. IR spectrum, ν , cm⁻¹: 1600, 1680, 1720, 1755. ¹H NMR spectrum (500 MHz, DMSO-d₆), δ, ppm: 0.83 (3H, s, CH₃); 1.39 (3H, s, CH₃); 1.45 (3H, s, CH₃); 1.50 (3H, s, CH₃); 6.19 (1H, s, -CH-O-); 7.58 (2H, t, C₆H₅); 7.75 (1H, t, C₆H₅); 8.13 (2H, d, C₆H₅). Found, %: C 70.16; H 6.49. C₁₆H₁₈O₄. Calculated, %: C 70.07; H 6.57.

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6-(4-Methylbenzoyl)-3,3,5,5-tetramethyl-2,3,5,6-tetrahydropyran-2,4-dione (4b). Yield 84%; mp 124-125°C. IR spectrum, v, cm⁻¹: 1615, 1690, 1720, 1755. ¹H NMR spectrum (60 MHz, CDCl₃), δ , ppm: 0.95 (3H, s, CH₃); 1.38 (3H, s, CH₃); 1.45 (3H, s, CH₃); 1.58 (3H, s, CH₃); 2.33 (3H, s, CH₃C₆H₄); 5.53 (1H, s, -CH-O-); 7.23 (2H, d, C₆H₄); 7.80 (2H, d, C₆H₄). Found, %: C 70.91; H 6.75. C₁₇H₂₀O₄. Calculated, %: C 70.83; H 6.94.

6-(4-Chlorobenzoyl)-3,3,5,5-tetramethyl-2,3,5,6-tetrahydropyran-2,4-dione (4c). Yield 86%; mp 125-126°C. IR spectrum, ν , cm⁻¹: 1595, 1690, 1720, 1765. ¹H NMR spectrum (60 MHz, CDCl₃), δ, ppm: 0.97 (3H, s, CH₃); 1.37 (3H, s, CH₃); 1.43 (3H, s, CH₃); 1.58 (3H, s, CH₃); 5.50 (1H, s, -CH–O–); 7.40 (2H, d, C₆H₄); 7.87 (2H, d, C₆H₄). Found, %: C 62.30; H 5.46. C₁₆H₁₇ClO₄. Calculated, %: C 62.24; H 5.51.

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