SYNTHESIS OF 1-ARYL-4,4,8,8-TETRAMETHYL-2,6-DIOXABICYCLO[3.3.0]-OCTA-3,7-DIONES

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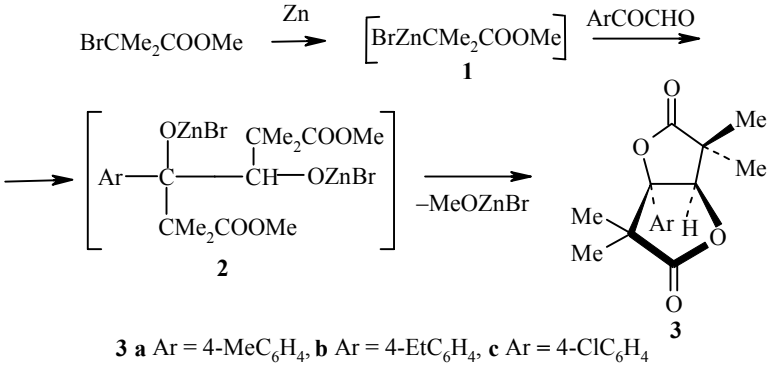
Keywords: arylglyoxal, 1-aryl-4,4,8,8-tetramethyl-2,6-dioxabicyclo[3.3.0]octa-3,7-dione, methyl 2-bromo-2-methylpropanoate, zinc, Reformatsky reaction.

Practically no information is available in the literature about the use of arylglyoxals in the Reformatsky reaction [1-3]. This is probably connected with the fact that, when arylglyoxals are present in the reaction medium (for example, ether–benzene), the first step of the Reformatsky reaction (the reaction of the 2-bromo-substituted alkanoate with zinc) does not proceed. We have revealed that in an ether–HMPA medium, the reaction of methyl 2-bromo-2-methylpropanoate with zinc and arylglyoxals is vigorous, leading to 1-aryl-4,4,8,8-tetramethyl-2,6-dioxabicyclo[3.3.0]octa-3,7-diones in high yields, according to the scheme:



3 a Ar = 4-MeC_6H_4, **b** Ar = 4-EtC_6H_4, **c** Ar = 4-ClC_6H_4

The Reformatsky reagent (**1**) formed as an intermediate reacts at both carbonyl groups of the arylglyoxal, yielding a bromozinc alcoholate (**2**), which spontaneously undergoes ring closure to the target bicycle (**3a-c**).

An MNDO quantum chemical calculation [4] of the geometry of molecule **3** (Ar = Ph) showed that the most stable structure is the "chair" type, which is probably the structure in which the synthesized compounds are formed.

1-(4-Tolyl)-4,4,8,8-tetramethyl-2,6-dioxabicyclo[3.3.0]octa-3,7-dione (3a). Yield 85%; mp 170-171°C. IR spectrum (vaseline oil), ν, cm^{-1}: 1615, 1790. ^1H NMR spectrum (60 MHz, $CDCl_3$), δ, ppm: 0.83 (3H, s, CH_3); 0.87 (3H, s, CH_3); 1.20 (3H, s, CH_3); 1.28 (3H, s, CH_3); 2.30 (3H, s, $\underline{CH_3}C_6H_4$); 5.03 (1H, s, –CH–O–); 7.17 (4H, s, C_6H_4). Found, %: C 70.51; H 6.85. $C_{17}H_{20}O_4$. Calculated, %: C 70.82; H 6.98.

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 0009-3122/01/3705-0650$25.00

1-(4-Ethylphenyl)-4,4,8,8-tetramethyl-2,6-dioxabicyclo[3.3.0]octa-3,7-dione (3b). Yield 77%; mp 120-121°C. IR spectrum (vaseline oil), ν, cm^{-1}: 1610, 1790. ^1H NMR spectrum (60 MHz, $CDCl_3$), δ, ppm: 0.85 (3H, s, CH_3); 0.89 (3H, s, CH_3); 1.17 (3H, t, $\underline{CH_3}CH_2$); 1.20 (3H, s, CH_3); 1.30 (3H, s, CH_3); 2.60 (2H, q, $CH_3\underline{CH_2}$); 5.00 (1H, s, –CH–O–); 7.17 (4H, s, C_6H_4). Found, %: C 71.39; H 7.20. $C_{18}H_{22}O_4$. Calculated, %: C 71.51; H 7.33.

1-(4-Chlorophenyl)-4,4,8,8-tetramethyl-2,6-dioxabicyclo[3.3.0]octa-3,7-dione (3c). Yield 68%; mp 221-222°C. IR spectrum (vaseline oil), ν, cm^{-1}: 1600, 1790. ^1H NMR spectrum (60 MHz, $CDCl_3$), δ, ppm; 0.87 (3H, s, CH_3); 0.90 (3H, s, CH_3); 1.22 (3H, s, CH_3); 1.33 (3H, s, CH_3); 5.03 (1H, s, –CH–O–); 7.33 (4H, s, C_6H_4). Found, %: C 62.12; H 5.43. $C_{16}H_{17}ClO_4$. Calculated, %: C 62.25; H 5.54.

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