

## Reactions of Dialkyl 4-Bromo-2,2-dimethyl-3-oxohexane-1,6-dioates, -heptane-1,7-dioates with Zinc and Aromatic Aldehydes

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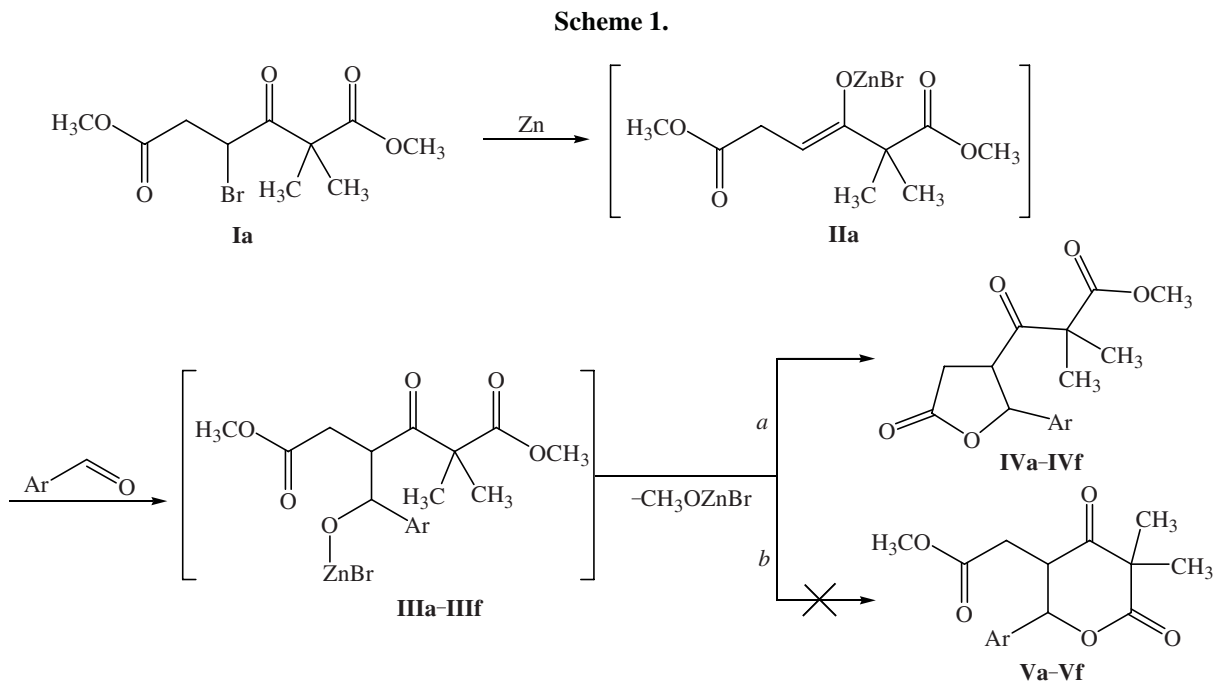
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**Abstract**—Zinc enolates generated from dimethyl 4-bromo-2,2-dimethyl-3-oxohexane-1,6-dioate and zinc reacted with aromatic aldehydes giving methyl 2,2-dimethyl-3-oxo-3-(5-oxo-2-aryltetrahydrofuran-3-yl)propanoates. The reaction of zinc enolates obtained from dimethyl 4-bromo-2,2-dimethyl-3-oxoheptane-1,7-dioate and zinc with aromatic aldehydes depending on the synthesis conditions led to the formation either methyl 2,2-dimethyl-3-oxo-3-(6-oxo-2-aryltetrahydropyran-3-yl)propanoates or 3-(5,5-dimethyl-4,6-dioxo-2-aryltetrahydropyran-3-yl)propanoates. The compounds synthesized formed as a single diastereomer of *E*-configuration.

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We formerly showed that reaction of zinc enolates prepared from alkyl 4-bromo-3-oxoalkanoates and zinc with aldehydes was a convenient preparation procedure for lactone structures, in particular, of substituted tetrahydropyran-2,4-diones [1]. In continuation of

studies in this field we investigated a reaction of dimethyl 4-bromo-2,2-dimethyl-3-oxohexane-1,6-dioate (**Ia**) with zinc and aromatic aldehydes. Presumably the reaction can take either of two routes *a* and *b* (Scheme 1).



Ar = Ph (**a**), 4-FC<sub>6</sub>H<sub>4</sub> (**b**), 4-ClC<sub>6</sub>H<sub>4</sub> (**c**), 4-BrC<sub>6</sub>H<sub>4</sub> (**d**), 3,4-(CH<sub>3</sub>O)<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (**e**), 3,4-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (**f**).

<sup>†</sup> Deceased.

In the first stage from the bromo derivative **Ia** and zinc formed zinc enolate **IIa** that reacted with aromatic aldehydes giving zinc bromide alcoholates **IIIa–IIIc**. Further an intramolecular cyclization of intermediates **IIIa–IIIc** can take the route *a* to form methyl 2,2-dimethyl-3-oxo-3-(5-oxo-2-aryltetrahydrofuran-3-yl)propanoates **IVa–IVf**, or the route *b* providing methyl (6-aryl-3,3-dimethyl-2,4-dioxo-2,3,5,6-tetrahydropyran-5-yl)ethanoates **Va–Vf**.

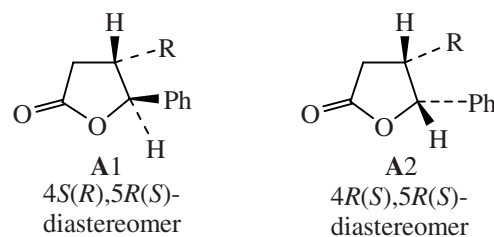
Disregarding the solvents used (ether–ethyl acetate, 1:3; ether–THF, 3:1; ether–HMPT 3:1) the reaction occurred along the route *a* leading to the substituted  $\gamma$ -lactones **IVa–IVf**. The composition and structure of compounds **IVa–IVf** were confirmed by elemental analyses,  $^1\text{H}$  NMR and IR spectra.

In the IR spectra the absorption bands of carbonyls from keto, ester, and lactone groups appear at 1720, 1750, and 1790  $\text{cm}^{-1}$  respectively. The most characteristic is the high frequency band at 1790  $\text{cm}^{-1}$ , inherent just to the carbonyl of a five-membered lactone ring [2]. In pyrandiones the lactone group carbonyl absorbs in the region 1745–1760  $\text{cm}^{-1}$  [1]. In the  $^1\text{H}$  NMR spectrum of methyl 2,2-dimethyl-3-oxo-3-[5-oxo-2-(4-bromophenyl)tetrahydrofuran-3-yl]propanoate (**IVd**) appear characteristic proton signals ( $\text{CDCl}_3$ , 300 MHz),  $\delta$ , ppm: 1.09 s (3H,  $\text{CH}_3$ ), 1.25 s (3H,  $\text{CH}_3$ ), 2.71 d.d (1H,  $\text{C}^3\text{H}_2$ ,  $J$  8.7, 10.5 Hz), 2.96 d.d (1H,  $\text{C}^3\text{H}_2$ ,  $J$  8.7, 10.5 Hz), 3.37 s (3H,  $\text{COOCH}_3$ ), 3.91 m (1H,  $\text{C}^4\text{H}$ ), 5.52 d (1H,  $\text{C}^5\text{H}$ ,  $J$  8.7 Hz).

The spectra of other compounds **IVa–IVc**, **IVe**, and **IVf** are analogous save the signals of aromatic protons. The cyclization direction was definitely proved by the

study of the reaction between the bromo derivative **Ib** with zinc and 4-bromobenzaldehyde. From the reaction products was isolated exclusively  $\gamma$ -lactone **IVd** (Scheme 2).

A single set of proton signals indicates that compounds **IVa–IVf** formed as an only of two possible diastereomers **A1** and **A2**. To elucidate its structure we calculated the enthalpy of formation  $\Delta H_f$  of dihedral angles  $\text{HC}^4\text{C}^5\text{H}$  in diastereomers **A1** and **A2** of compound **IVa** by the method SCF MO LCAO in MNDO-PM3 approximation [3].

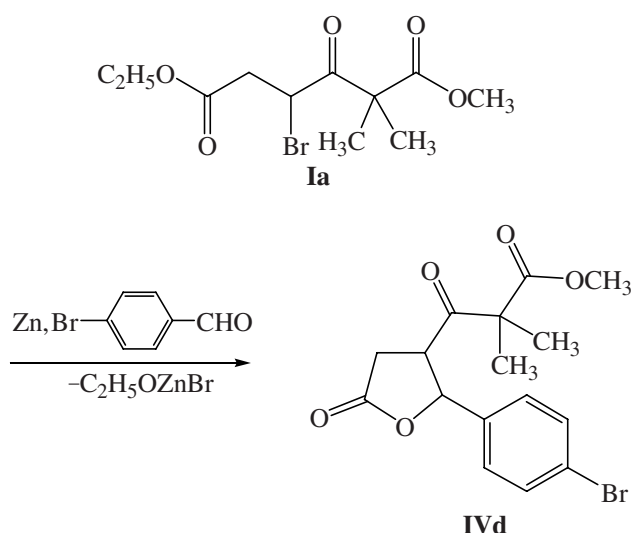


$^3J_{4,5}(\text{exp.}), \text{Hz}$	8.7	8.7
$\Delta H_f, \text{kcal/mol}$	-184.02	-179.9
$\text{HC}^4\text{C}^5\text{H}, \text{deg}$	-140.30	29.60
$\Delta H_f, \text{kcal/mol}$	-184.03	-180.60
$\text{HC}^4\text{C}^5\text{H}, \text{deg}$	-138.51	17.52
$^3J_{4,5}(\text{calc.}), \text{Hz}$	8.4	10.1

Preliminary known experimental value  $^3J_{4,5}(\text{exp})$  was 8.7 Hz, and applying Karplus equation with Bothner-By parameters [4] we found that in structures **A1** and **A2** the dihedral angles  $\text{HC}^4\text{C}^5\text{H}$  should be 140.30 and 29.60° respectively. Settling these values for the angles in structures **A1** and **A2** we carried out the calculation of their heats of formation  $\Delta H_f$ . The calculations showed that molecule **A1** is more stable than **A2** by  $\sim 4.7 \text{ kcal mol}^{-1}$ . Further with these values of dihedral angles established we performed calculation of the structures **A1** and **A2** with a complete geometry optimization.

For the revealed most stable conformers the potential curves were drawn describing the dependence of conformers enthalpy on the dihedral angle of fragments rotation around the bond  $\text{C}^4\text{--COC}(\text{CH}_3)_2\text{COOCH}_3$ . From the minima on the potential curve the most stable conformers were found with heats of formation  $-184.03$  (**A1**) and  $-180.60 \text{ kcal mol}^{-1}$  (**A2**). Therewith the dihedral angles  $\text{HC}^4\text{C}^5\text{H}$  in molecules **A1** and **A2** proved to be equal to  $-138.51$  and  $17.52 \text{ deg}$  respectively. Applying again the Karplus equation with Bothner-By parameters we found that theoretically obtained value  $^3J_{4,5}(\text{teor})$  for diastereomer **A1** was 8.4 Hz, and for diastereomer **A2**,

Scheme 2.



10.1 Hz. The close values of  $^3J_{4,5}(\text{exp})$  and  $^3J_{4,5}(\text{teor})$  for diastereomer **A1** evidence the formation of compound **IVa** as also compounds **IVb–IVf** in the form of diastereomer **A1**.

The reaction of dimethyl 4-bromo-2,2-dimethyl-3-oxoheptane-1,7-dioate (**VIa**) with zinc and aromatic aldehydes also can take two routes *a* and *b* (Scheme 3).

In the first stage from the bromo derivative **VIa** and zinc formed zinc enolate **VIIa** that reacted with aromatic aldehydes giving zinc bromide alcoholates **VIIIa–VIIIc**. The latter in their turn may undergo cyclization along the route *a* forming  $\delta$ -lactones **IXa** and **IXb**, or by the route *b* giving substituted tetrahydropyran-2,4-diones **Xa** and **Xb**. The study demonstrated that the reaction result is governed by the nature of the solvent used in the process. The reaction carried out in the mixture ether–ethyl acetate, 1:1, occurred by the route *a* leading to the formation of methyl 2,2-dimethyl-3-oxo-3-(6-oxo-2-aryltetrahydropyran-3-yl)propanoates **IXa** and **IXb**.

The composition and structure of compounds **IXa** and **IXb** were confirmed by elemental analyses,  $^1\text{H}$  NMR and IR spectra. The IR spectra contain absorption bands of keto ( $1710\text{ cm}^{-1}$ ), ester, and lactone groups ( $\sim 1745\text{ cm}^{-1}$ ). In the  $^1\text{H}$  NMR spectrum of methyl 2,2-dimethyl-3-oxo-3-[6-oxo-2-(4-bromophenyl)tetrahydropyran-3-yl]propanoate (**IXa**) appear characteristic proton

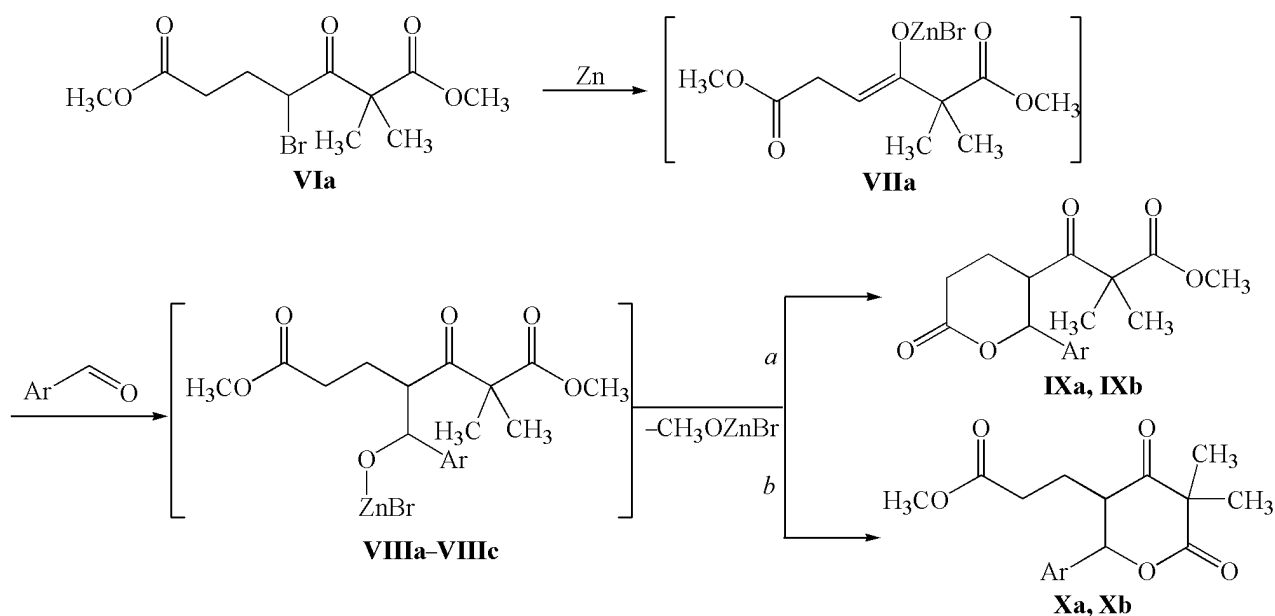
signals ( $\text{CDCl}_3$ , 100 MHz),  $\delta$ , ppm: 0.71 s (3H,  $\text{CH}_3$ ), 1.09 s (3H,  $\text{CH}_3$ ), 2.05 m, 2.60 m (4H,  $\text{C}^3\text{H}_2$ ,  $\text{C}^4\text{H}_2$ ), 3.20 m (1H,  $\text{C}^5\text{H}$ ), 3.40 s (3H,  $\text{COOCH}_3$ ), 5.53 d (1H,  $\text{C}^6\text{H}$ ,  $J$  9.9 Hz). A characteristic feature of  $^1\text{H}$  NMR spectra of  $\delta$ -lactones **IXa** and **IXb**, like that of the spectra of  $\gamma$ -lactones **IVa–IVf** is the presence in the strong field of sharply differing proton signals ( $\Delta\delta \approx 0.3\text{ ppm}$ ) belonging to magnetically nonequivalent methyl groups  $\text{CMe}_2$ . The chemical shifts of protons from the methoxy-carbonyl groups virtually completely coincide (see EXPERIMENTAL).

In order to establish the spatial structure of diastereomers **IXa** and **IXb** we performed a quantum-chemical calculation of a model compound, methyl 2,2-dimethyl-3-oxo-3-(6-oxo-2-phenyl-tetrahydropyran-3-yl)propanoate by the procedure used for compound **IVa**.

The data obtained, namely,  $\Delta H_f$  at fixed angles  $\text{HC}^5\text{C}^6\text{H}$ , and also  $^3J_{5,6}(\text{teor})$  prove the formation of compounds **IXa** and **IXb** in a structure **B1**.

The reaction carried out in a mixture ether–THF, 1:1, occurred with cyclization along the route *b* and led to the formation of substituted tetrahydropyran-2,4-diones **Xa** and **Xb** whose composition and structure were confirmed by elemental analyses,  $^1\text{H}$  NMR and IR spectra. The IR spectra contain absorption bands of keto ( $1710\text{ cm}^{-1}$ ), ester, and lactone groups ( $\sim 1750\text{ cm}^{-1}$ ). In

Scheme 3.



**VIII**, Ar = 4-ClC<sub>6</sub>H<sub>4</sub> (**a**), 4-BrC<sub>6</sub>H<sub>4</sub> (**b**), 3,4-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (**c**); **IX**, Ar = 4-BrC<sub>6</sub>H<sub>4</sub> (**a**), 3,4-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (**b**); **X**, Ar = 4-ClC<sub>6</sub>H<sub>4</sub> (**a**), 4-BrC<sub>6</sub>H<sub>4</sub> (**b**).

the  $^1\text{H}$  NMR spectrum of methyl 1-[5,5-dimethyl-4,6-dioxo-2-(4-bromophenyl)tetrahydropyran-3-yl]propanoate (**Xb**) characteristic proton signals are present ( $\text{CDCl}_3$ , 300 MHz),  $\delta$ , ppm: 1.41 s (3H,  $\text{CH}_3$ ), 1.44 s (3H,  $\text{CH}_3$ ), 1.78 m (2H,  $\text{CH}_2\text{C}^5$ ), 2.22 m (2H,  $\text{CH}_3\text{OOCCH}_2$ ,  $\text{C}^4\text{H}_2$ ), 2.95 m (1H,  $\text{C}^5\text{H}$ ), 3.54 s (3H,  $\text{COOCH}_3$ ), 5.08 d (1H,  $\text{C}^6\text{H}$ ,  $J$  10.5 Hz).

In contrast to the  $^1\text{H}$  NMR spectra of  $\delta$ -lactones **IXa** and **IXb** in the spectra of pyrandiones **Xa** and **Xb** the proton signals of methyl groups appear in weaker field (~1.40, 1.45 ppm) and do not significantly differ. The protons of methoxycarbonyl group give rise to a resonance at ~3.55 ppm. The  $^1\text{H}$  NMR spectra are consistent with the previously published findings [1]. For instance, in the  $^1\text{H}$  NMR spectrum of 5-ethyl-3,3-dimethyl-6-phenyltetrahydropyran-2,4-dione singlets from the protons of  $\text{CMe}_2$  group are located at 1.31 and 1.37 ppm, and the doublet of the proton from the  $\text{CHPh}$  moiety, at 5.20 ppm ( $J$  11 Hz).

It was also shown in [1] that pyrandiones with  $^3J_{5,6}$  11 Hz were *E*-isomers, and those with  $^3J_{5,6}$  1–4 Hz, *Z*-isomers. In the spectra of compounds **Xa** and **Xb**  $^3J_{5,6}$  is 10.5 Hz proving their *E*-configuration. The quantum-chemical calculation of two possible diastereomers carried out as described above by an example of methyl 3-(5,5-dimethyl-4,6-dioxo-2-phenyltetrahydropyran-3-yl)propanoate also indicated the formation of compounds **Xa** and **Xb** in a structure **C1**.

## EXPERIMENTAL

IR spectra of individual compounds were recorded from mulls in mineral oil on spectrophotometers UR-20 (**IVa–IVf**) and Specord 75IR (**Xb** and **Xc**).  $^1\text{H}$  NMR spectra were registered from solutions in  $\text{CDCl}_3$  for compounds **IVb**, **IVf**, **IXa**, **Xa**, and **Xc** on a spectrometer Tesla BS-567A (100 MHz), for compound **Xb** on a spectrometer Mercury Plus-300 (300 MHz), internal reference HMDS. The  $^1\text{H}$  NMR spectra of compounds **IVa**, **IVc–IVe**, **IXb** were measured in  $\text{DMSO}-d_6$  on a spectrometer Bruker DRX-500 (500 MHz).

**Methyl 2,2-dimethyl-3-oxo-3-(2-aryl-5-oxotetrahydrofuran-3-yl)propanoates IVa–IVf.** To 0.1 mol of fine zinc turnings in a mixed solvent (ether–ethyl acetate, 1:3; ether–THF, 3:1; ether–HMPT, 3:1) was added 0.007 mol of dimethyl 4-bromo-3-oxo-hexane-1,6-dioate and 0.007 mol of aromatic aldehyde in 5 ml of solvent. To start the reaction the mixture was heated and maintained at 50–55°C for 40 min. Then the mixture was

cooled, hydrolyzed with 10% solution of HCl, the reaction products were extracted into ether, the extract was dried with sodium sulfate, and the solvent was distilled off. The residue was twice recrystallized from  $\text{CCl}_4$ .

**Methyl 2,2-dimethyl-3-oxo-(5-oxo-2-phenyl-tetrahydrofuran-3-yl)propanoate (IVa).** Yield 1.32 g (65%), mp 90–92°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1720, 1750, 1790.  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 1.06 s (3H,  $\text{CH}_3$ ), 1.24 s (3H,  $\text{CH}_3$ ), 2.71 d.d (1H,  $\text{C}^3\text{H}_2$ ,  $J$  8.7, 10.5 Hz), 2.97 d.d (1H,  $\text{C}^3\text{H}_2$ ,  $J$  8.7, 10.5 Hz), 3.32 s (3H,  $\text{COOCH}_3$ ), 3.91 m (1H,  $\text{C}^4\text{H}$ ), 5.51 d (1H,  $\text{C}^5\text{H}$ ,  $J$  8.7 Hz), 7.36–7.45 m (5H,  $\text{C}_6\text{H}_5$ ). Found, %: C 66.11; H 6.19.  $\text{C}_{16}\text{H}_{18}\text{O}_5$ . Calculated, %: C 66.19; H 6.25.

**Methyl 2,2-dimethyl-3-oxo-3-[5-oxo-2-(4-fluorophenyl)-tetrahydrofuran-3-yl]propanoate (IVb).** Yield 1.36 g (63%), mp 74–75°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1720, 1750, 1790.  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 0.99 s (3H,  $\text{CH}_3$ ), 1.22 s (3H,  $\text{CH}_3$ ), 2.72 d, 2.73 d (2H,  $\text{C}^3\text{H}_2$ ,  $J$  9.0, 11.0 Hz), 3.33 s (3H,  $\text{COOCH}_3$ ), 3.48 m (1H,  $\text{C}^4\text{H}$ ), 5.48 d (1H,  $\text{C}^5\text{H}$ ,  $J$  8.7 Hz), 6.80–7.20 m (4H, 4- $\text{FC}_6\text{H}_4$ ). Found, %: C 62.25; H 5.49.  $\text{C}_{16}\text{H}_{17}\text{FO}_5$ . Calculated, %: C 62.33; H 5.56.

**Methyl 2,2-dimethyl-3-oxo-3-[5-oxo-2-(4-chlorophenyl)-tetrahydrofuran-3-yl]propanoate (IVc).** Yield 1.36 g (60%), mp 95–96°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1720, 1750, 1790.  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 1.09 s (3H,  $\text{CH}_3$ ), 1.24 s (3H,  $\text{CH}_3$ ), 2.71 d.d (1H,  $\text{C}^3\text{H}_2$ ,  $J$  8.7, 10.5 Hz), 2.97 d.d (1H,  $\text{C}^3\text{H}_2$ ,  $J$  8.7, 10.5), 3.37 s (3H,  $\text{COOCH}_3$ ), 3.92 m (1H,  $\text{C}^4\text{H}$ ), 5.53 d (1H,  $\text{C}^5\text{H}$ ,  $J$  8.7 Hz), 7.41 d, 7.49 d (4H, 4- $\text{ClC}_6\text{H}_4$ ,  $J$  8.0 Hz). Found, %: C 59.09; H 5.22.  $\text{C}_{16}\text{H}_{17}\text{ClO}_5$ . Calculated, %: C 59.17; H 5.28.

**Methyl 2,2-dimethyl-3-oxo-3-[5-oxo-2-(4-bromophenyl)-tetrahydrofuran-3-yl]propanoate (IVd).** Yield 1.60 g (62%), mp 100–102°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1720, 1750, 1790.  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 1.09 s (3H,  $\text{CH}_3$ ), 1.25 s (3H,  $\text{CH}_3$ ), 2.71 d.d (1H,  $\text{C}^3\text{H}_2$ ,  $J$  8.7, 10.5 Hz), 2.96 d.d (1H,  $\text{C}^3\text{H}_2$ ,  $J$  8.7, 10.5 Hz), 3.37 s (3H,  $\text{COOCH}_3$ ), 3.91 m (1H,  $\text{C}^4\text{H}$ ), 5.52 d (1H,  $\text{C}^5\text{H}$ ,  $J$  8.7 Hz), 7.35 d, 7.63 d (4H, 4- $\text{BrC}_6\text{H}_4$ ,  $J$  8.0 Hz). Found, %: C 51.97; H 4.58.  $\text{C}_{16}\text{H}_{17}\text{BrO}_5$ . Calculated, %: C 52.05; H 4.64.

**Methyl 2,2-dimethyl-3-oxo-3-[5-oxo-2-(3,4-dimethoxyphenyl)-tetrahydrofuran-3-yl]-propanoate (IVe).** Yield 1.25 g (51%), mp 110–112°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1720, 1750, 1790.  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 1.06 s (3H,  $\text{CH}_3$ ), 1.23 s (3H,  $\text{CH}_3$ ), 2.71 d.d (1H,  $\text{C}^3\text{H}_2$ ,  $J$  8.7, 10.5 Hz), 2.94 d.d (1H,  $\text{C}^3\text{H}_2$ ,  $J$  8.7, 10.5 Hz), 3.39 s (3H,  $\text{COOCH}_3$ ), 3.74 s (3H,  $\text{OCH}_3$ ), 3.77 s (3H,

OCH<sub>3</sub>), 3.96 m (1H, C<sup>4</sup>H), 5.41 d (1H, C<sup>5</sup>H, *J* 8.7 Hz), 6.87 d [1H, 3,4-(CH<sub>3</sub>O)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>], 6.94 d [1H, 3,4-(CH<sub>3</sub>O)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>], 7.04 s [1H, 3,4-(CH<sub>3</sub>O)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]. Found, %: C 61.74; H 6.27. C<sub>18</sub>H<sub>22</sub>O<sub>7</sub>. Calculated, %: C 61.71; H 6.33.

**Methyl 2,2-dimethyl-3-oxo-3-[5-oxo-2-(3,4-dichlorophenyl)tetrahydrofuran-3-yl]-propanoate (IVf).** Yield 1.66 g (66%), mp 105–106°C. IR spectrum, ν, cm<sup>-1</sup>: 1720, 1750, 1790. <sup>1</sup>H NMR spectrum, δ, ppm: 1.06 s (3H, CH<sub>3</sub>), 1.23 s (3H, CH<sub>3</sub>), 2.73 d, 2.74 d (2H, C<sup>3</sup>H<sub>2</sub>, *J* 9.0, 11.0 Hz), 3.40 s (3H, COOCH<sub>3</sub>), 3.59 m (1H, C<sup>4</sup>H), 5.81 d (1H, C<sup>5</sup>H, *J* 8.7 Hz), 7.12–7.30 m (3H, 3,4-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>). Found, %: C 53.41; H 4.42. C<sub>16</sub>H<sub>16</sub>Cl<sub>2</sub>O<sub>5</sub>. Calculated, %: C 53.50; H 4.49.

**Methyl 2,2-dimethyl-3-oxo-3-(6-oxo-2-aryl-tetrahydropyran-3-yl)propanoates IXa and IXb** were obtained analogously to compounds IVa–IVf. Solvent ether–benzene, 1:1.

**Methyl 2,2-dimethyl-3-oxo-3-[6-oxo-2-(4-bromophenyl)tetrahydropyran-3-yl]propanoate (IXa).** Yield 1.37 g (51%), mp 110–112°C. IR spectrum, ν, cm<sup>-1</sup>: 1705, 1745. <sup>1</sup>H NMR spectrum, δ, ppm: 0.71 C (3H, CH<sub>3</sub>), 1.09 C (3H, CH<sub>3</sub>), 2.05 m, 2.60 m (4H, C<sup>3</sup>H<sub>2</sub>, C<sup>4</sup>H<sub>2</sub>), 3.20 m (1H, C<sup>5</sup>H), 3.40 C (3H, COOCH<sub>3</sub>), 5.53 d (1H, C<sup>6</sup>H, *J* 9.7 Hz), 6.98 d, 7.33 d (4H, 4-BrC<sub>6</sub>H<sub>4</sub>, *J* 8.0 Hz). Found, %: C 53.26; H 4.93. C<sub>17</sub>H<sub>19</sub>BrO<sub>5</sub>. Calculated, %: C 53.28; H 5.00.

**Methyl 2,2-dimethyl-3-oxo-3-[6-oxo-2-(3,4-dichlorophenyl)tetrahydropyran-3-yl]propanoate (IXb).** Yield 1.44 g (55%), mp 118–119°C. IR spectrum, ν, cm<sup>-1</sup>: 1705, 1745. <sup>1</sup>H NMR spectrum, δ, ppm: 1.02 s (3H, CH<sub>3</sub>), 1.10 s (3H, CH<sub>3</sub>), 1.99 m, 2.07 m, 2.68 m (4H, C<sup>3</sup>H<sub>2</sub>, C<sup>4</sup>H<sub>2</sub>), 3.47 s (3H, COOCH<sub>3</sub>), 3.83 m (1H, C<sup>5</sup>H), 5.86 d (1H, C<sup>6</sup>H, *J* 9.7 Hz), 7.52 d, 7.61 d, 7.64 s (3H, 3,4-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>). Found, %: C 54.64; H 4.79. C<sub>17</sub>H<sub>18</sub>Cl<sub>2</sub>O<sub>5</sub>. Calculated, %: C 54.71; H 4.86.

**Methyl 3-(5,5-dimethyl-4,6-dioxo-2-aryltetrahydropyran-3-yl)propanoates Xa and Xb** were obtained analogously to compounds IVa–IVf. Solvent ether–THF, 1:3.

**Methyl 3-[5,5-dimethyl-4,6-dioxo-2-(4-chlorophenyl)tetrahydropyran-3-yl]propanoate (Xa).** Yield 1.63 g (69%), mp 136–137°C. IR spectrum, ν, cm<sup>-1</sup>: 1710, 1750. <sup>1</sup>H NMR spectrum, δ, ppm: 1.44 s (3H, CH<sub>3</sub>), 1.46 s (3H, CH<sub>3</sub>), 1.80 m (2H, CH<sub>2</sub>C<sup>5</sup>), 2.27 m (2H, CH<sub>3</sub>OOCCH<sub>2</sub>, C<sup>4</sup>H<sub>2</sub>), 2.97 m (1H, C<sup>5</sup>H), 3.55 s (3H, COOCH<sub>3</sub>), 5.10 d (1H, C<sup>6</sup>H, *J* 10.2 Hz), 7.14–7.38 m (4H, 4-ClC<sub>6</sub>H<sub>4</sub>). Found, %: C 60.18; H 5.58. C<sub>17</sub>H<sub>19</sub>ClO<sub>5</sub>. Calculated, %: C 60.27; H 5.65.

**Methyl 3-[5,5-dimethyl-4,6-dioxo-2-(4-bromophenyl)tetrahydropyran-3-yl]propanoate (Xb).** Yield 1.90 g (71%), mp 140°C. IR spectrum, ν, cm<sup>-1</sup>: 1710, 1750. <sup>1</sup>H NMR spectrum, δ, ppm: 1.41 s (3H, CH<sub>3</sub>), 1.44 s (3H, CH<sub>3</sub>), 1.78 m (2H, CH<sub>2</sub>C<sup>5</sup>), 2.22 m (2H, CH<sub>3</sub>OOCCH<sub>2</sub>, C<sup>4</sup>H<sub>2</sub>), 2.95 m (1H, C<sup>5</sup>H), 3.54 s (3H, COOCH<sub>3</sub>), 5.08 d (1H, C<sup>6</sup>H, *J* 10.5 Hz), 7.22 d, 7.51 d (4H, 4-BrC<sub>6</sub>H<sub>4</sub>, *J* 8.7 Hz). Found, %: C 53.20; H 4.91. C<sub>17</sub>H<sub>19</sub>BrO<sub>5</sub>. Calculated, %: C 53.28; H 5.00.

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