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## LETTERS TO THE EDITOR

# Reaction of Alicyclic Reformatsky Reagents with 2-Arylmethylene-1,3-diphenylpropane-1,3-diones

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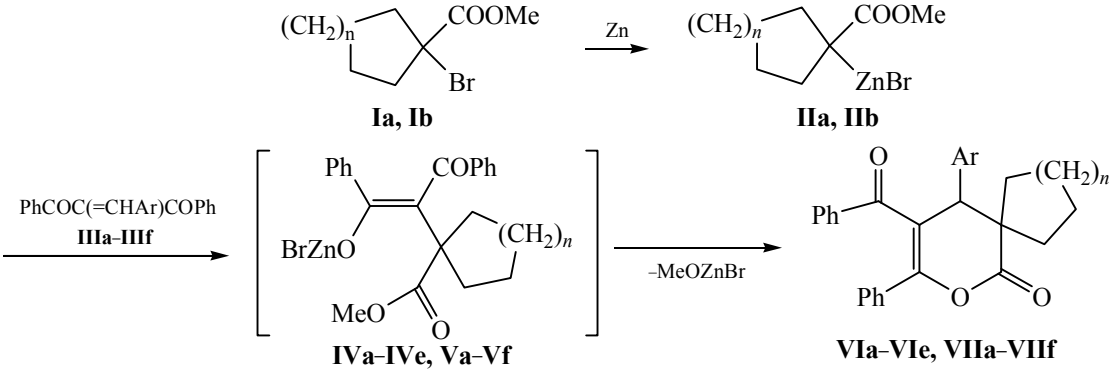
Previously we found that the reaction of alicyclic Reformatsky reagents with 1,3-diarylprop-2-ene-1-ones resulted in the substituted spirodihydropyranones [1, 2]. In continuation of these studies we examined the reaction of the Reformatsky reagents **IIa** and **IIb** derived from methyl 1-bromocycloalkylcarboxylates **Ia** and **Ib** and zinc with 2-arylmethylene-1,3-diphenylpropane-1,3-dione **IIIa–IIIf**. Our study showed that addition of the organozinc reagents **IIa–IIb** to the unsaturated diketones **IIIa–IIIf** occurs in 1,4-position to form the intermediates **IVa–IVe**, **Va–Vf** followed by the cyclization with the release of bromozinc methylate to form 10-aryl-9-benzoyl-8-phenyl-7-oxaspiro[4.5]dec-8-ene-6-ones **VIa–VIf** and 5-aryl-4-benzoyl-3-phenyl-2-oxaspiro[5.5]undec-3-ene-1-ones **VIIa–VIIf**, respectively.




*n* = 1 (**Ia, IIa, IV, VI**), 2 (**Ib, IIb, V, VII**). **III–VII**, Ar = 4-$BrC_6H_4$ (**a**), 4-$ClC_6H_4$ (**b**), 3-$BrC_6H_4$ (**c**), 2,4-$Cl_2C_6H_3$ (**d**), 2-Cl-4-$FC_6H_3$ (**e**); **III, V, VII**, Ar = 4-$FC_6H_4$ (**f**).

The composition and structure of the compounds obtained were confirmed by the elemental analysis, IR and $^1$H NMR spectroscopy data. The IR spectra of compounds **VIa–VIe**, **VIIa–VIIf** contain the characteristic bands of C=C bonds at 1610–1625 $cm^{-1}$ and of the ketone and lactone carbonyl groups at 1630–1640 and 1765–1790 $cm^{-1}$. In the $^1$H NMR spectra there is one set of signals, among which the most characteristic is a singlet of methine proton in the range of 4.00–4.87 ppm.

The IR spectra of compounds **VIa–VIe**, **VIIa–VIIf** were obtained on a Specord-75IR spectrophotometer as mulls in mineral oil. The $^1$H NMR spectra of $CDCl_3$ solutions of these compounds are recorded on a Fourier spectrometer TESLA BS-567A (100 MHz) with internal reference TMS.

**10-Aryl-9-benzoyl-8-phenyl-7-oxaspiro[4.5]dec-8-ene-6-ones (VIa–VIe).** A mixture of 1.5 g of fine zinc turnings, a catalytic amount of mercuric chloride, 5 mmol of 1,5-diaryl-1,4-pentadiene-3-one, 5.3 mmol of methyl 1-bromocyclopentylcarboxylate, 20 ml of benzene, 5 ml of ethyl acetate, 1 ml of HMPT was refluxed for 4 h, cooled, decanted from excess zinc, and quenched with 5% hydrochloric acid. The organic layer was separated, and the reaction products were extracted twice with ethyl acetate. After drying the

extract with anhydrous sodium sulfate the solvent was evaporated, and the compounds **VIa-VIe** were recrystallized from ethyl acetate.

**9-Benzoyl-10-(4-bromophenyl)-8-phenyl-7-oxaspiro[4.5]dec-8-ene-6-one (VIa).** Yield 0.88 g (36%), mp 164–165°C. IR spectrum, ν, $cm^{-1}$: 1620 (C=C), 1635 (C=O, ketone), 1775 (C=O, lactone). $^1H$ NMR spectrum, δ, ppm: 1.40–2.20 m [8H, $(CH_2)_4$], 4.13 s (1H, $C^{10}H$), 7.10–7.42 m (14H, Ar). Found, %: C 68.80; H 4.89; Br 16.61. $C_{28}H_{23}BrO_3$. Calculated, %: C 69.00; H 4.76; Br 16.39.

**9-Benzoyl-8-phenyl-10-(4-chlorophenyl)-7-oxaspiro[4.5]dec-8-ene-6-one (VIb).** Yield 0.91 g (41%), mp 160–161ºC. IR spectrum, ν, $cm^{-1}$: 1620 (C=C), 1635 (C=O, ketone), 1775 (C=O, lactone). $^1H$ NMR, δ, ppm: 1.20–2.25 m [8H, $(CH_2)_4$], 4.02 s (1H, $C^{10}H$), 6.75–7.40 m (14H, Ar). Found, %: C 76.15; H 5.11; Cl 8.19. $C_{28}H_{23}ClO_3$. Calculated, %: C 75.93; H 5.23; Cl 8.00.

**9-Benzoyl-10-(3-bromophenyl)-8-phenyl-7-oxaspiro[4.5]dec-8-ene-6-one (VIc).** Yield 1.05 g (43%), mp 171–172ºC. IR spectrum, ν, $cm^{-1}$: 1625 (C=C), 1635 (C=O, ketone), 1775 (C=O, lactone). $^1H$ NMR spectrum, δ, ppm: 1.20–2.25 m [8H, $(CH_2)_4$], 4.00 s (1H, $C^{10}H$), 6.90–7.45 m (14H, Ar). Found, %: C 69.26; H 4.58; Br 16.47. $C_{28}H_{23}BrO_3$. Calculated, %: C 69.00; H 4.76; Br 16.39.

**9-Benzoyl-10-(2,4-dichlorophenyl)-8-phenyl-7-oxaspiro[4.5]dec-8-ene-6-one (VId).** Yield 0.76 g (32%), mp 181–182ºC. IR spectrum, ν, $cm^{-1}$: 1625 (C=C), 1640 (C=O, ketone), 1765 (C=O, lactone). $^1H$ NMR spectrum, δ, ppm: 1.15–2.35 m [8H, $(CH_2)_4$], 4.78 s (1H, $C^{10}H$), 6.82–7.48 m (13H, Ar). Found, %: C 70.69; H 4.77; Cl 14.68. $C_{28}H_{22}Cl_2O_3$. Calculated, %: C 70.45; H 4.65; Cl 14.85.

**9-Benzoyl-8-phenyl-10-(4-fluoro-2-chlorophenyl)-7-oxaspiro[4.5]dec-8-ene-6-one (VIe).** Yield 0.85 g (37%), mp 157–158ºC. IR spectrum, ν, $cm^{-1}$: 1610 (C=C), 1635 (C=O, ketone), 1765 (C=O, lactone). $^1H$ NMR, δ, ppm: 1.35–2.32 m [8H, $(CH_2)_4$], 4.78 s (1H, $C^{10}H$), 6.80–7.45 m (13H, Ar). Found, %: C 73.18; H 5.00; Cl 7.52. $C_{28}H_{22}ClFO_3$. Calculated, %: C 72.96; H 4.81; Cl 7.69.

**5-Aryl-4-benzoyl-3-phenyl-2-oxaspiro[5.5]undec-3-ene-1-ones (VIIa-VIIf)** were obtained similarly starting from methyl 1-bromocyclohexanecarboxylate.

**4-Benzoyl-5-(4-bromophenyl)-3-phenyl-2-oxaspiro[5.5]undec-3-ene-1-one (VIIa).** Yield 1.38 g (55%), mp 179–180ºC. IR spectrum, ν, $cm^{-1}$: 1625 (C=C), 1635 (C=O, ketone), 1785 (C=O, lactone). $^1H$ NMR spectrum, δ, ppm: 1.10–2.25 m [10H, $(CH_2)_5$], 4.18 s (1H, $C^5H$), 6.80–7.40 m (14H, Ar). Found, %: C 69.71; H 4.86; Br 16.13. $C_{29}H_{25}BrO_3$. Calculated, %: C 69.47; H 5.03; Br 15.94.

**4-Benzoyl-3-phenyl-5-(4-chlorophenyl)-2-oxaspiro[5.5]undec-3-ene-1-one (VIIb).** Yield 1.17 g (51%), mp 152–153ºC. IR spectrum, ν, $cm^{-1}$: 1620 (C=C), 1640 (C=O, ketone), 1780 (C=O, lactone). $^1H$ NMR spectrum, δ, ppm: 1.08–2.26 m [10H, $(CH_2)_5$], 4.22 s (1H, $C^5H$), 6.85–7.40 m (14H, Ar). Found, %: C 76.37; H 5.35; Cl 7.59. $C_{29}H_{25}ClO_3$. Calculated, %: C 76.22; H 5.51; Cl 7.76.

**4-Benzoyl-5-(3-bromophenyl)-3-phenyl-2-oxaspiro[5.5]undec-3-ene-1-one (VIIc).** Yield 1.10 g (44%), mp 174–175ºC. IR spectrum, ν, $cm^{-1}$: 1625 (C=C), 1635 (C=O, ketone), 1790 (C=O, lactone). $^1H$ NMR spectrum, δ, ppm: 1.10–2.20 m [10H, $(CH_2)_5$], 4.24 s (1H, $C^5H$), 6.94–7.44 m (14H, Ar). Found, %: C 69.38; H 4.97; Br 15.78. $C_{29}H_{25}BrO_3$. Calculated, %: C 69.47; H 5.03; Br 15.94.

**4-Benzoyl-5-(2,4-dichlorophenyl)-3-phenyl-2-oxaspiro[5.5]undec-3-ene-1-one (VIId).** Yield 0.69 g (28%), mp 173–174ºC. IR spectrum, ν, $cm^{-1}$: 1615 (C=C), 1635 (C=O, ketone), 1775 (C=O, lactone). $^1H$ NMR spectrum, δ, ppm: 1.10–2.20 m [10H, $(CH_2)_5$], 4.19 s (1H, $C^5H$), 6.85–7.40 m (13H, Ar). Found, %: C 70.98; H 4.81; Cl 14.30. $C_{29}H_{24}Cl_2O_3$. Calculated, %: C 70.88; H 4.92; Cl 14.43.

**4-Benzoyl-3-phenyl-5-(4-fluoro-2-chlorophenyl)-2-oxaspiro[5.5]undec-3-ene-1-one (VIIe).** Yield 0.85 g (37%), mp 157–158ºC. IR spectrum, ν, $cm^{-1}$: 1620 (C=C), 1640 (C=O, ketone), 1770 (C=O, lactone). $^1H$ NMR spectrum, δ, ppm: 1.20–2.40 m [10H, $(CH_2)_5$], 4.87 s (1H, $C^5H$), 6.80–7.45 m (13H, Ar). Found, %: C 73.56; H 5.18; Cl 7.36. $C_{29}H_{24}ClFO_3$. Calculated, %: C 73.34; H 5.09; Cl 7.46.

**4-Benzoyl-3-phenyl-5-(4-fluorophenyl)-2-oxaspiro[5.5]undec-3-ene-1-one (VIIf).** Yield 0.95 g (43%), mp 207–208ºC. IR spectrum, ν, $cm^{-1}$: 1625 (C=C), 1635 (C=O, ketone), 1775 (C=O, lactone). $^1H$ NMR spectrum, δ, ppm: 1.20–2.10 m [10H, $(CH_2)_5$], 4.16 s (1H, $C^5H$), 7.02–7.60 m (14H, Ar). Found, %: C 79.28; H 5.90. $C_{29}H_{25}FO_3$. Calculated, %: C 79.07; H 5.72.

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