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Reaction of 1,5-Diarylpenta-1,4-dien-3-ones with Methyl 1-Bromocycloalkanecarboxylates and Zinc

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Abstract—Methyl 1-bromocyclopentane-, 1-bromocyclohexane- and 1-bromocycloheptanecarboxylates react with zinc and 1,5-diarylpenta-1,4-dien-3-ones to form 10-aryl-8-(2-arylethenyl)-7-oxaspiro[4.5]dec-8-en-6-ones, 5-aryl-3-(2-arylethenyl)-2-oxaspiro[5.5]undec-3-en-1-ones, and 5-aryl-3-(2-arylethenyl)-2-oxaspiro[5.6]-dodec-3-en-1-ones, respectively.

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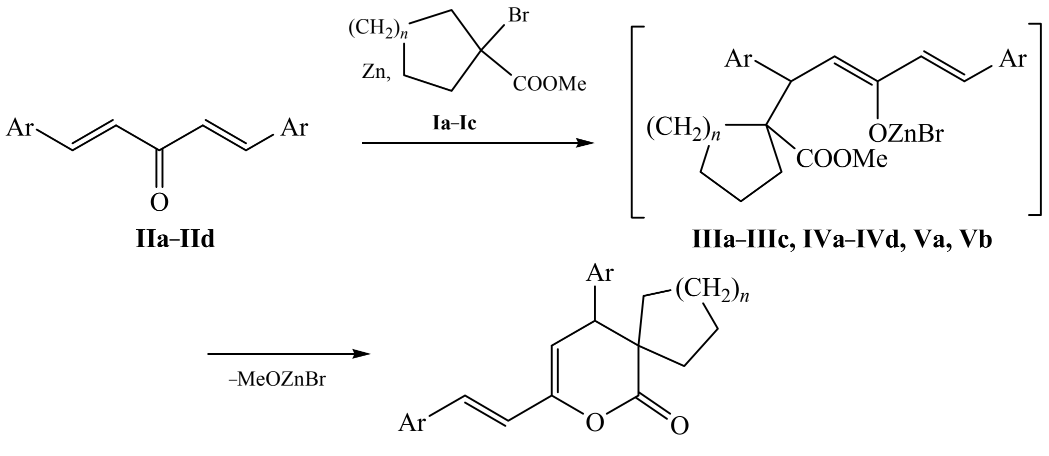
Previously we found that the reaction of alicyclic Reformatsky reagents with 1,3-diarylprop-2-ene-1-ones affords substituted spirodihydropyranones [1, 2]. Continuing these studies, we investigated the reaction of Reformatsky reagents derived from methyl 1-bromocycloalkanecarboxylates (**Ia–Ic**) with zinc and 1,5-diarylpenta-1,4-dien-3-ones (**IIa–IId**). According to our research, the organozinc reagents formed added to compounds (**IIa–IId**) in 1,4-position of C=C–C=O fragment with the formation of intermediates (**IIIa–IIIc, IVa–IVd, Va**, and **Vb**). In the course of the reaction, these intermediates undergo cyclization due to the attack of the oxygen atom on the carbonyl carbon atom of the ester group with the cleavage of bromozinc methoxide, affording substituted spirodihydropyran-2-ones, namely, 10-aryl-8-(2-arylethenyl)-7-oxaspiro[4.5]dec-8-en-6-ones (**VIa–VIc**), 5-aryl-3-(2-arylethenyl)-2-oxaspiro[5.5]undeca-3-en-1-ones (**VIIa–VIId**), and 5-aryl-3-(2-arylethenyl)-2-oxaspiro[5.6]dodec-3-en-1-ones (**VIIIa, VIIIb**).



VIa–VIc, VIIa–VIId, VIIIa, VIIIb

I: n = 1 (**a**), 2 (**b**), 3 (**c**); **II**: Ar = Ph (**a**), 4-ClC_6H_4 (**b**), 4-$MeOC_6H_4$ (**c**), 4-BrC_6H_4 (**d**); **III, VI**: n = 1; Ar = Ph (**a**), 4-ClC_6H_4 (**b**), 4-$MeOC_6H_4$ (**c**); **IV, VII**: n = 2; Ar = Ph (**a**), 4-ClC_6H_4 (**b**), 4-$MeOC_6H_4$ (**c**), 4-BrC_6H_4 (**d**); **V, VIII**: n = 3; Ar = Ph (**a**), 4-BrC_6H_4 (**b**).

The composition and structure of the compounds obtained were confirmed by elemental analysis, IR and ^{1}H NMR spectroscopy. The IR spectra of compounds **VIa–VIc, VIIa–VIId, VIIIa,** and **VIIIb** include characteristic bands of C=C bonds at 1655–1665 cm^{-1} and of lactone carbonyl groups at 1755–1770 cm^{-1}. In the ^{1}H NMR spectra there is one set of signals, among which are the characteristic doublets of the dihydropyran ring protons at 3.30–3.79 and 5.37–5.70 ppm and doublets of protons of vinyl fragment at 6.35–6.85 and 6.92–7.12 ppm with spin–spin coupling constants 15–16 Hz, which correspond to the *E*-isomers.

EXPERIMENTAL

The IR spectra of compounds **VIa–VIc, VIIa–VIId, VIIIa,** and **VIIIb** were obtained on a spectrophotometer Specord-75IR from mulls in mineral oil. The ^{1}H NMR spectra of solutions in $CDCl_3$ of these compounds were recorded on a Mercury Plus-300 (300 MHz) spectrometer, internal reference TMS.

10-Aryl-8-(2-arylethenyl)-7-oxaspiro[4.5]dec-8-en-6-ones (VIa–VIc). In a round-bottom 250 ml flask fitted with a reflux condenser were placed 1.5 g of fine zinc turnings, a catalytic amount of mercuric chloride, 5 mmol of 1,5-diaryl-1,4-pentadien-3-one, 5.1 mmol of methyl 1-bromocyclopentanecaroboxylate, 20 ml of benzene, 5 ml of ethyl acetate, and 1 ml of hexamethyltriamidophosphate. The reaction mixture was refluxed for 2 h, then cooled, the liquid was decanted from excess zinc, and decomposed with 5% hydrochloric acid. The organic layer was separated from the water layer, and the reaction products were extracted twice with ethyl acetate. After drying the extract with anhydrous sodium sulfate, the solvents were distilled off, and compound **VIa–VIc** were recrystallized from ethyl acetate.

10-Phenyl-8-(2-phenylethenyl)-7-oxaspiro[4.5]-dec-8-en-6-one (VIa). Yield 0.79 g (48%), mp 150–151ºC. IR spectrum, ν, cm^{-1}: 1665 (C=C), 1770 (C=O). ^{1}H NMR spectrum, δ, ppm: 1.26–2.13 m [8H, $(CH_2)_4$], 3.36 d (1H, C^{10}H, J 6.3 Hz), 5.52 d (1H,=C^{9}H, *J* 6.3 Hz), 6.48 d, 7.12 d (2H, CH=CH, *J* 15.9 Hz), 7.11 d, 7.21–7.36 m, 7.43 d (10H, 2Ph, *J* 7.2 Hz), Found, %: C 83.81, H 6.62. $C_{23}H_{22}O_2$. Calculated, %: C 83.60, H 6.71.

10-(4-Chlorophenyl)-8-[2-(4-chlorophenyl)ethenyl]-7-oxaspiro[4.5]dec-8-en-6-one (VIb). Yield 0.78 g (39%), mp 204–205ºC. IR spectrum, ν, cm^{-1}: 1655 (P=C), 1760 (C=O). ^{1}H NMR spectrum, δ, ppm: 1.28–2.12 m [8H $(CH_2)_4$], 3.35 d (1H, C^{10}H, *J* 6.6 Hz), 5.51 d (1H,=C^{9}H, *J* 6.6 Hz), 6.45 d, 7.06 d (2H, CH=CH, *J* 15.6 Hz), 7.04 d, 7.25 d, 7.30 d, 7.37 d [8H, 2(4-ClC_6H_4), *J* 8.4 Hz]. Found, %: C 68.97, H 5.16; Cl 17.92. $C_{23}H_{20}Cl_2O_2$. Calculated, %: C 69.18, H 5.05, Cl 17.76.

10-(4-methoxyphenyl)-8-[2-(4-methoxyphenyl)-ethenyl]-7-oxaspiro[4.5]dec-8-en-6-one (VIc). Yield 1.03 g (52%), mp 130–131ºC. IR spectrum, ν, cm^{-1}: 1660 (P=C), 1760 (C=O). ^{1}H NMR spectrum, δ, ppm: 1.32–2.10 m [8H, $(CH_2)_4$], 3.30 d (1H, C^{10}H, *J* 6.5 Hz), 3.76 s (3H, OMe), 3.81 s (3H, OMe), 5.46 d (1H, =C^{9}H, *J* 6.5 Hz), 6.36 d , 7.06 d (2H, CH=CH, *J* 16.2 Hz), 6.81 d, 6.87 d, 7.03 d, 7.38 d [8H, 2(4-$MeOC_6H_4$), *J* 8.4 Hz]. Found, %: C 77.05, H 6.83. $C_{25}N_{26}O_4$. Calculated, %: C 76.90, H 6.71.

5-Aryl-3-(2-arylethenyl)-2-oxaspiro[5.5]undec-3-en-1-ones (VIIa–VIId) were prepared similarly to compounds **VI**. Methyl 1-bromocyclohyxylcarboxylate was used as initial compound.

5-Phenyl-3-(2-phenylethenyl)-2-oxaspiro[5.5]-undeca-3-ene-1-one (VIIa). Yield 1.05 g (61%), mp 110–111ºC. IR spectrum, ν, cm^{-1}: 1655 (C=C), 1765 (C=O). ^{1}H NMR spectrum, δ, ppm: 1.07–2.10 m [10H, $(CH_2)_5$], 3.49 d (1H, C^{5}H, *J* 6.5 Hz), 5.46 d (1H, =C^{4}H, *J* 6.5 Hz), 6.48 d, 7.10 d (2H, CH=CH, *J* 15.6 Hz), 7.11 d, 7.22–7.30 m, 7.34 m, 7.44 d (10H, 2Ph, *J* 6.9 Hz). Found, %: P 83.81, H 6.90. $C_{24}H_{24}O_2$. Calculated, %: P 83.69, H 7.02.

5-(4-Chlorophenyl)-3-[2-(4-chlorophenyl)ethenyl]-2-oxaspiro[5.5]undec-3-en-1-one (VIIb). Yield 1.10 g (53%), mp 175–176ºC. IR spectrum, ν, cm^{-1}: 1655 (C=C), 1770 (C=O). ^{1}H NMR spectrum, δ, ppm: 1.05–1.95 m [10H, $(CH_2)_5$], 3.79 d (1H, C^{5}H, *J* 6.5 Hz), 5.70 d (1H, =C^{4}H, *J* 6.5 Hz), 6.85 d, 6.92 d (2H, CH=CH, *J* 15.6 Hz), 7.13 d, 7.39 d, 7.42 d, 7.60 d [8H, 2(4-ClC_6H_4), *J* 8.4 Hz]. Found, %: C 69.91, H 5.45; Cl 16.97. $C_{24}H_{22}Cl_2O_2$. Calculated, %: C 69.74, H 5.36; Cl 17.15.

5-(4-Methoxyphenyl)-3-[2-(4-methoxyphenyl)-ethenyl]-2-oxaspiro[5.5]undec-3-en-1-one (VIIc). Yield 0.96 g (47%), mp 148–149ºC. IR spectrum, ν, cm^{-1}: 1655 (C=C), 1755 (C=O). ^{1}H NMR spectrum, δ, ppm: 6.1–2.10 m [10H, $(CH_2)_5$], 3.43 d (1H, C^{5}H, *J* 6.6 Hz), 3.76 s (3H, OMe), 3.81 s (3H, OMe), 5.38 d (1H, =C^{4}H, *J* 6.6 Hz), 6.35 d, 7.03 d (2H, CH=CH, *J* 16.2 Hz), 6.85 d, 6.87 d, 7.02 d, 7.37 d [8H, 2(4-$MeOC_6H_4$), *J* 7.4 Hz]. Found, %: C 77.38, H 6.84. $C_{26}H_{28}O_4$. Calculated, %: C 77.20, H 6.98.

5-(4-Bromophenyl)-3-[2-(4-bromophenyl)ethenyl]-2-oxaspiro[5.5]undec-3-en-1-one (VIId). Yield 1.24 g (49%), mp 204–206ºC. IR spectrum, ν, cm^{-1}: 1655 (C=C), 1770 (C=O). ^1H NMR spectrum, δ, ppm: 1.04–2.10 m [10H, $(CH_2)_5$], 3.46 d (1H, C^5H, *J* 6.6 Hz), 5.43 d (1H, =C^4H, *J* 6.6 Hz), 6.45 d, 7.02 d (2H, CH=CH, *J* 16.2 Hz), 6.97 d, 7.29 d, 7.40 d, 7.46 d [8H, 2(4-BrC_6H_4), *J* 8.4 Hz]. Found, %: C 57.64, H 4.55; Br 31.56. $C_{24}H_{22}Br_2O_2$. Calculated, %: C 57.39, H 4.42; Br 31.82.

5-Aryl-3-(2-arylethenyl)-2-oxaspiro[5.6]dodecyl-3-en-1-ones (VIIIa, VIIIb) were obtained similarly to compounds **VI**. Methyl 1-bromocycloheptanecarboxylate was used as initial compound.

5-Phenyl-3-(2-phenylethenyl)-2-oxaspiro[5.6]-dodecyl-3-en-1-one (VIIIa). Yield 0.97 g (54%), mp 99–100ºC. IR spectrum, ν, cm^{-1}: 1655 (C=C), 1770 (C=O). ^1H NMR spectrum, δ, ppm: 1.14–2.10 m [12H, $(CH_2)_6$], 3.44 d (1H, C^5H, *J* 6.6 Hz), 5.45 d (1H, =C^4H, *J* 6.6 Hz), 6.47 d, 7.10 d (2H, CH=CH, *J* 16.2 Hz), 7.09 d, 7.22–7.37 m, 7.43 d (10H, 2Ph, *J* 7.2 Hz). Found, %: C 83.92, H 7.46. $C_{25}H_{26}O_2$. Calculated, %: C 83.76, H 7.31.

5-(4-Bromophenyl)-3-[2-(4-bromophenyl)ethenyl]-2-oxaspiro[5.6]dodecyl-3-en-1-one (VIIIb). Yield 1.26 g (49%), mp 204–206ºC. IR spectrum, ν, cm^{-1}: 1660 (C=C), 1770 (C=O). ^1H NMR spectrum, δ, ppm: 1.00–2.10 m [12H, $(CH_2)_6$], 3.38 d (1H, C^5H, *J* 6.6 Hz), 5.37 d (1H, =C^4H, *J* 6.6 Hz), 6.36 d, 6.96 d (2H, CH=CH, *J* 16.2 Hz), 6.88 d, 7.21 d, 7.34 d, 7.39 d [8H, 2(4-BrC_6H_4), *J* 8.4 Hz]. Found, %: C 58.39, H 4.78; Br 30.66. $C_{25}H_{24}Br_2O_2$. Calculated, %: C 58.16, H 4.69; Br 30.95.

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