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Reaction of Substituted Chalcones with Methyl 1-Bromocycloalkanecarboxylates and Zinc

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Abstract—Methyl 1-bromocyclopentane- and 1-bromocyclobutanecarboxylates react with zinc and substituted chalcones to form spiro-3,4-dihydropyran-2-one derivatives: 8, 10-diaryl-7-oxaspiro[4.5]dec-8-en-6-ones and 7,9-diaryl-6-oxaspiro[3.5]non-7-en-5-ones, respectively.

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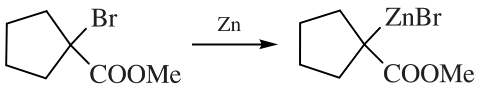
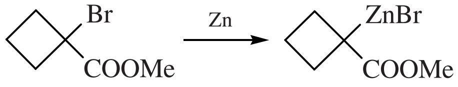
When reacted with α,β-unsaturated ketones, Reformatsky reagents add across both 1,2 and 1,4 positions of the conjugated system, and the 1,4-adducts undergo cyclization affording unsaturated lactones, specifically dihydropyran-2-one derivatives [1].

We carried out reactions of methyl 1-bromocyclopentane- and 1-bromocyclobutanecarboxy-lates with zinc and substituted chalcones to obtain similar compounds with a spiro-carbon atom. Refor-matsky reagents **I** and **II** are formed by the reaction of these bromoesters with zinc.

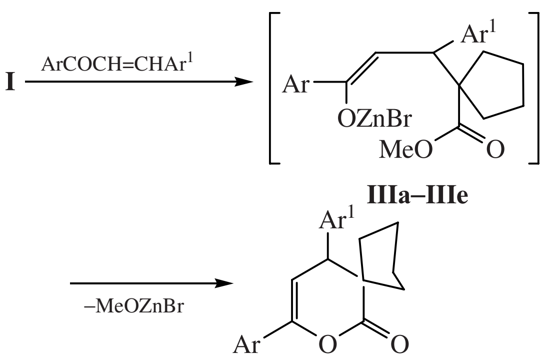


I



II

Reformatsky reagent **I** adds to chalcones across the 1,4 position to give intermediates **IIIa–IIIe**. Under the reaction conditions, these intermediates exert cyclization as a result of the attack of oxygen on the ester carbonyl carbon to form substituted spiro-3,4-dihydropyran-2-ones, namely 8,10-diaryl-7-oxaspiro [4.5]dec-8-en-6-ones **IVa–IVe**.

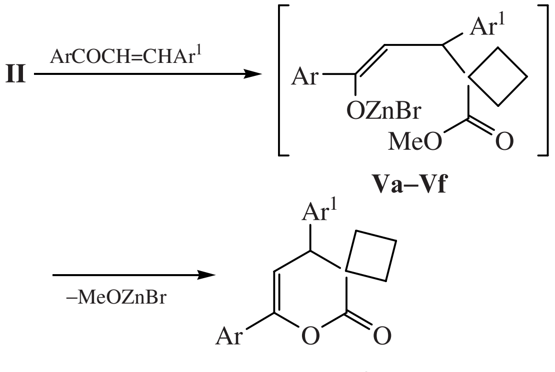


IIIa–IIIe

IVa–IVe

III, IV, Ar = Ph, Ar^1 = Ph (**a**), 4-ClC$_6$H$_4$ (**b**), 4-BrC$_6$H$_4$ (**c**); Ar = 4-BrC$_6$H$_4$, Ar^1 = Ph (**d**); Ar = 4-MeOC$_6$H$_4$, Ar^1 = 4-ClC$_6$H$_4$ (**e**).

Reformatsky reagent **II** reacts with substituted chalcones in the same way to form intermediates **Va–Vf** and then spiro-3,4-dihydropyran-2-ones, namely 7,9-diaryl-6-oxaspiro[3.5]non-7-en-5-ones **VIa–VIf**.



Va–Vf

VIa–VIf

V, VI, Ar = Ph, Ar^1 = Ph (**a**), 4-ClC$_6$H$_4$ (**b**), 4-BrC$_6$H$_4$ (**c**); Ar = 4-BrC$_6$H$_4$, Ar^1 = Ph (**d**); Ar = Ph, Ar^1 = 4-MeOC$_6$H$_4$ (**e**); Ar = Ar^1 = 4-ClC$_6$H$_4$ (**f**).

The yields of the final products were 43–72%. The composition and structure of compounds **IVa–IVe** and **VIa–VIf** were confirmed by elemental analysis and IR and ^{1}H NMR spectroscopy. The IR spectra show characteristic absorption bands of the carbonyl group at 1740–1770 cm^{-1} and the C=C bond at 1635–1675cm^{-1}. The ^{1}H NMR spectra contain signals of the aryl protons at 6.70–7.72 ppm, doublets of the double-bond protons at 5.80–5.92 ppm, doublets of the methine protons at 3.37–3.45 ppm (**IV**) and 3.65–3.70 ppm (**VI**), and signals of the cyclohexene ring protons at 0.91–2.25 ppm.

EXPERIMENTAL

The IR spectra were recorded on a Specord-75IR spectrophotometer (vaseline oil). The ^{1}H NMR spectra were measured on a TESLA BS-576A spectrometer (100 MHz) in $CDCl_3$ against internal HMDS.

8,10-Diaryl-7-oxaspiro[4,5]dec-8-en-6-ones IVa–IVe. A mixture of 11 mmol of methyl 1-bromocyclopentanecarboxylate and 10 mmol of the corresponding chalcone in 20 ml of absolute benzene was added to a mixture of 1.5 g of finely zinc turnings, a catalytic quantity of mercuric chloride, 1 ml of HMPA, and 11 ml of anhydrous ethyl acetate. The reaction mixture was refluxed for 2 h, cooled, filtered, and hydrolyzed with 5% acetic acid. The organic layer was separated, and the aqueous layer was extracted with two portions of ethyl acetate. The combined extract was dried with anhydrous sodium sulfate, the solvent was evaporated, and compounds **IVa–IVe** were recrystallized from ethyl acetate.

8,10-Diphenyl-7-oxaspiro[4.5]dec-8-en-6-one (IVa). Yield 1.55 g (51%), mp 115–116°C. IR spectrum, ν, cm^{-1}: 1645 (C=C), 1755 (C=O). ^{1}H NMR spectrum, δ, ppm: 6.97–7.68 m (10H, 2Ph), 5.92 d (1H, =CH, *J* 6.5 Hz), 3.38 d (1H, ArC*H*, *J* 6.5 Hz), 1.10–2.22 m [8H, $(CH_2)_4$]. Found, %: C 83.08; H 6.56. $C_{21}H_{20}O_2$. Calculated, %: C 82.86; H 6.62.

10-(4-Chlorophenyl)-8-phenyl-7-oxaspiro[4.5]dec-8-en-6-one (IVb). Yield 1.59 g (47%), mp 110–111°C. IR spectrum, ν, cm^{-1}: 1655 (C=C), 1755 (C=O). ^{1}H NMR spectrum, δ, ppm: 6.94–7.53 m (9H, Ph, 4-ClC_6H_4), 5.91 d (1H, =CH, *J* 6.5 Hz), 3.37 d (1H, ArC*H*, *J* 6.5 Hz), 1.20–2.19 m [8H, $(CH_2)_4$]. Found, %: C 74.21; H 5.48; Cl 10.68. $C_{21}H_{19}ClO_2$. Calculated, %: C 74.44; H 5.65; Cl 10.46.

10-(4-Bromophenyl)-8-phenyl-7-oxaspiro[4.5]dec-8-en-6-one (IVc). Yield 1.63 g (48%), mp 111–112°C. IR spectrum, ν, cm^{-1}: 1655 (C=C), 1740 (C=O). ^{1}H NMR spectrum, δ, ppm: 6.87–7.72 m (9H, Ph, 4-BrC_6H_4), 5.91 d (1H, =CH, *J* 6.5 Hz), 3.37 d (1H, ArC*H*, *J* 6.5 Hz), 0.96–2.21 m [8H, $(CH_2)_4$]. Found, %: C 65.66; H 5.12; Br 20.59. $C_{21}H_{19}BrO_2$. Calculated, %: C 65.81; H 5.00; Br 20.85.

8-(4-Bromophenyl)-10-phenyl-7-oxaspiro[4.5]dec-8-en-6-one (IVd). Yield 1.52 g (45%), mp 113–114°C. IR spectrum, ν, cm^{-1}: 1635 (C=C), 1770 (C=O). ^{1}H NMR spectrum, δ, ppm: 6.93–7.58 m (9H, Ph, 4-BrC_6H_4), 5.91 d (1H, =CH, *J* 6.5 Hz), 3.39 d (1H, ArC*H*, *J* 6.5 Hz), 1.20–2.22 m [8H, $(CH_2)_4$]. Found, %: C 66.01; H 5.08; Br 20.72. $C_{21}H_{19}BrO_2$. Calculated, %: C 65.81; H 5.00; Br 20.85.

10-(4-Chlorophenyl)-8-(4-methoxyphenyl)-7-oxaspiro[4.5]dec-8-en-6-one (IVe). Yield 1.57 g (43%), mp 118–119°C. IR spectrum, ν, cm^{-1}: 1640 (C=C), 1760 (C=O). ^{1}H NMR spectrum, δ, ppm: 7.50 d, 7.24 d, 6.96 d, 6.74 d (8H, 4-$MeOC_6H_4$, 4-ClC_6H_4, *J* 8.5 Hz), 5.80 d (1H, =CH, *J* 6.5 Hz), 3.71 s (3H, MeO), 3.45 d (1H, ArC*H*, *J* 6.5 Hz), 1.00-2.20 m [8H, $(CH_2)_4$]. Found, %: C 71.45; H 5.61; Cl 9.49. $C_{22}H_{21}ClO_3$. Calculated, %: C 71.64; H 5.74; Cl 9.61.

7,9-Diaryl-6-oxaspiro[3.5]non-7-en-5-ones VIa-VIf were obtained analogously to compounds **IVa-IVe** starting from methyl 1-bromocyclobutanecarboxylate.

7,9-Diphenyl-6-oxaspiro[3.5]non-7-en-5-one (VIa). Yield 1.97 g (68%), mp 110–111°C. IR spectrum, ν, cm^{-1}: 1665 (C=C), 1750 (C=O). ^{1}H NMR spectrum, δ, ppm: 6.98–7.70 m (10H, 2Ph), 5.85 d (1H, =CH, *J* 6.5 Hz), 3.69 d (1H, ArC*H*, *J* 6.5 Hz), 1.78–2.56 m [6H, $(CH_2)_3$]. Found, %: C 83.00; H 6.38. $C_{20}H_{18}O_2$. Calculated, %: C 82.73; H 6.25.

9-(4-Chlorophenyl)-7-phenyl-6-oxaspiro[3.5]non-7-en-5-one (VIb). Yield 2.18 g (67%), mp 104–105°C. IR spectrum, ν, cm^{-1}: 1650 (C=C), 1760 (C=O). ^{1}H NMR spectrum, δ, ppm: 6.91–7.67 m (9H, Ph, 4-ClC_6H_4), 5.83 d (1H, =CH, *J* 6.5 Hz), 3.67 d (1H, ArC*H*, *J* 6.5 Hz), 1.80-2.57 m [6H, $(CH_2)_3$]. Found, %: C 74.12; H 5.17; Cl 11.09. $C_{20}H_{17}ClO_2$. Calculated, %: C 73.96; H 5.28; Cl 10.91.

9-(4-Bromophenyl)-7-phenyl-6-oxaspiro[3.5]non-7-en-5-one (VIc). Yield 2.59 g (70%), mp 137–138°C. IR spectrum, ν, cm^{-1}: 1675 (C=C), 1760 (C=O). ^{1}H NMR spectrum, δ, ppm: 6.97–7.52 m (9H, Ph, 4-BrC_6H_4), 5.86 d (1H, =CH, *J* 6.5 Hz), 3.70 d (1H, ArC*H*, *J* 6.5 Hz), 1.80–2.57 m [6H, $(CH_2)_3$]. Found, %: C 64.89; H 4.52; Br 21.45. $C_{20}H_{17}BrO_2$. Calculated, %: C 65.05; H 4.64; Br 21.64.

7-(4-Bromophenyl)-9-phenyl-6-oxaspiro[3.5]non-7-en-5-one (VId). Yield 2.59 g (70%), mp 133–134°C. IR spectrum, ν, cm^{-1}: 1645 (C=C), 1740 (C=O). ^{1}H NMR spectrum, δ, ppm: 7.10–7.66 m, 6.94 d (9H, Ph, 4-BrC_6H_4, *J* 8.4 Hz), 5.81 d (1H, =CH, *J* 6.5 Hz), 3.65 d (1H, ArC*H*, *J* 6.5 Hz), 1.77–2.60 m [6H, $(CH_2)_3$]. Found, %: C 65.12; H 4.83; Br 21.91. $C_{20}H_{17}BrO_2$. Calculated, %: C 65.05; H 4.64; Br 21.64.

9-(4-Methoxyphenyl)-7-phenyl-6-oxaspiro[3.5]non-7-en-5-one (VIe). Yield 2.31 g (72%), mp 89–90°C. IR spectrum, ν, cm^{-1}: 1635 (C=C), 1745 (C=O). ^{1}H NMR spectrum, δ, ppm: 7.20-7.67 m, 7.02 d, 6.72 d (9H, 4-$MeOC_6H_4$, Ph, *J* 8.4 Hz), 5.86 d (1H, =CH, *J* 6.5 Hz), 3.71 s (3H, MeO), 3.65 d (1H, ArC*H*, *J* 6.5 Hz), 1.81-2.55 m [6H, $(CH_2)_3$]. Found, %: C 78.48; H 6.11. $C_{21}H_{20}O_3$. Calculated, %: C 78.73; H 6.29.

7,9-Bis(4-chlorophenyl)-6-oxaspiro[3.5]non-7-en-5-one (VIf). Yield 1.34 g (65%), mp 118–119°C. IR spectrum, ν, cm^{-1}: 1660 (C=C), 1765 (C=O). ^{1}H NMR spectrum, δ, ppm: 7.59 d, 7.27 d, 7.20 d, 6.91 d (8H, 4-ClC_6H_4, 4-ClC_6H_4, *J* 8.5 Hz), 5.82 d (1H, =CH, *J* 6.5 Hz), 3.68 d (1H, ArC*H*, *J* 6.5 Hz), 1.74–2.58 m [6H, $(CH_2)_3$]. Found, %: C 67.08; H 4.67; Cl 19.4. $C_{20}H_{16}Cl_2O_2$. Calculated, %: C 66.87; H 4.49; Cl 19.74.

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