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Zirconium-catalyzed one-pot synthesis of *ε*-spirocyclopropyl-*ε*-caprolactones

Leila O. Khafizova,* Rinat R. Gubaidullin, Natal'ya R. Popod'ko,
Ekaterina S. Meshcheryakova, Leonard M. Khalilov and Usein M. Dzhemilev

Institute of Petrochemistry and Catalysis, Russian Academy of Sciences, 450075 Ufa, Russian Federation.
Fax: +7 347 284 2750; e-mail: khafizovaleila@gmail.com

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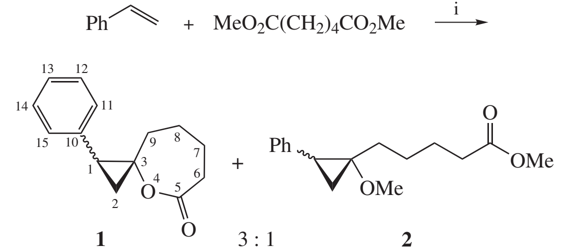
A new one-pot synthesis of *ε*-spirocyclopropyl-*ε*-caprolactones has been implemented *via* the reaction between vinylarenes, $EtAlCl_2$ and dimethyl adipate catalyzed by Cp_2ZrCl_2 in 60% yield.

Investigations into the search of simple and convenient synthetic approaches towards various classes of heterocyclic compounds including spiroheterocycles is one of the major trends in development of modern organic chemistry.[1–9] Spiroheterocyclic fragments, in particular, those containing lactone rings, are known to be the structural components of many natural and synthetic compounds possessing biological activity.[10–12]

Recently, we reported that the interaction between vinylarenes and Cl_nAlEt_{3-n} (n = 1–3) in the presence of carboxylates and magnesium metal under the action of a Cp_2ZrCl_2 catalyst affords a stereoisomeric 1-alkoxy-1-alkyl-2-arylcyclopropanes.[13,14] Herein, we have extended these investigations and report the versatile combinations which opens an access to *ε*-spirocyclopropyl-*ε*-caprolactones.

Our study of the cyclopropanation reaction[13,14] involving α,ω-dicarboxylates, styrene and $EtAlCl_2$ revealed that the change in the length of the hydrocarbon chain between the ester groups surprisingly contributes to the formation of the end products. In this sense, of particular interest was dimethyl adipate. Thus, its reaction with styrene and $EtAlCl_2$ in the presence of Cp_2ZrCl_2 catalyst (styrene : diester : [Al] : Mg : [Zr] = 2 : 1 : 4 : 4 : 0.1, THF, 20 °C, 8 h) afforded 1-phenyl-4-oxaspiro[2.6]nonan-5-one **1** (*ε*-spirocyclopropyl-*ε*-caprolactone) along with a small amount of methyl 5-(1-methoxy-2-phenylcyclopropyl)pentanoate **2** (3 : 1 ratio) in a total yield of 80% (Scheme 1).[†]

The structures of the isolated compounds were determined by means of NMR, IR spectroscopy and chromato-mass spectrometry. The ^1H and ^{13}C NMR spectra of **1** and **2** contain two sets of signals (1:1 ratio) that confirm the presence of *cis* and *trans* stereoisomers.



1 *cis*/*trans* (1:1) 3 : 1 **2** *cis*/*trans* (1:1)

Scheme 1 *Reagents and conditions*: i, $EtAlCl_2$, Mg, Cp_2ZrCl_2, THF, 20 °C, 8 h.

The ^{13}C NMR signals at δ 65.50 (65.75) (C^3) and 176.08 (176.41) (C^5) attributable to the spiro carbon atom and the carbonyl moiety were characteristic of spirolactone **1**, whereas in the 2D HMBC experiment the first signal correlated with the ^1H NMR

[†] *General experimental procedure.* A pre-calcined and argon-filled 50 ml glass reactor equipped with magnetic stirrer, reflux condenser and thermometer was charged with THF (15 ml), $EtAlCl_2$ (40 mmol), dimethyl adipate (10 mmol), magnesium powder (40 mmol), Cp_2ZrCl_2 (1.0 mmol), and vinylarene (20 mmol) under a dried argon atmosphere at 0 °C. The reaction mixture was allowed to warm to room temprature (20–22 °C) and was stirred for 8 h. Then the reaction mixture was quenched with 7–10% HCl. The organic layer was separated. The aqueous layer was extracted with diethyl ether (2×20 ml). The combined extracts and the organic layer were neutralized with $NaHCO_3$ and dried over $MgSO_4$. The products were isolated by column chromatography (silica gel L, 180/250 μ) using hexane–ethyl acetate (50 : 1) as eluent. Structural assignments for *cis* and *trans* stereoisomers were made on the basis of spectral data for fractions enriched in one of the isomers.

1-Phenyl-4-oxaspiro[2.6]nonan-5-one **1**, *cis–trans* isomer mixture. Yield 62%, R_f 0.48 (hexane–ethyl acetate, 1:1). IR (KBr, ν/cm^{-1}): 3458, 3027, 2936, 2862, 1741, 1603, 1498, 1435, 1328, 1282, 1195, 1094, 1015, 922, 881, 830, 776, 700, 671, 607, 514. MS, m/z: 216 [M]$^+$. Found (%): C, 77.59; H, 7.43. Calc. for $C_{14}H_{16}O_2$ (%): C, 77.75; H, 7.46.

For *cis*-**1**. ^1H NMR (400 MHz, $CDCl_3$) δ: 1.32 (m, 1H, CH_2 cyclopropane ring), 1.49 (m, 1H, CH_2, cyclopropane ring), 1.53 (m, 2H, CH_2), 1.56 (m, 1H, CH_2), 1.63–1.92 (m, 2H, CH_2), 1.83 (m, 1H, CH_2), 2.67 (dd, 1H, CH cyclopropane ring, $^3J_{trans}$ 8.0 Hz, $^3J_{cis}$ 10.0 Hz), 2.78 (m, 2H, CH_2), 7.17–7.38 (m, 5H, Ph). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 17.52, 22.93, 26.27, 30.11, 30.70, 35.45, 65.50, 126.79, 128.26, 128.53, 136.33, 176.41.

For *trans*-**1**. ^1H NMR (400 MHz, $CDCl_3$) δ: 1.33 (m, 1H, CH_2 cyclopropane ring), 1.54 (m, 1H, CH_2 cyclopropane ring), 1.63–1.92 (m, 2H, CH_2), 1.69 (m, 1H, CH_2), 1.77 (m, 1H, CH_2), 1.88 (m, 1H, CH_2), 2.23 (m, 1H, CH cyclopropane ring), 2.25 (m, 1H, CH_2), 2.78 (m, 2H, CH_2), 7.17–7.38 (m, 5H, Ph). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.19, 22.59, 27.21, 29.36, 35.49, 36.19, 65.75, 126.53, 127.76, 128.42, 135.85, 176.08.

Methyl 5-(1-methoxy-2-phenylcyclopropyl)pentanoate **2**, *cis–trans* isomer mixture. Yield 18%, R_f 0.67 (hexane–ethyl acetate, 1:1). IR (KBr, ν/cm^{-1}): 3458, 3025, 2936, 2863, 2827, 1738, 1603, 1498, 1437, 1363, 1247, 1172, 1067, 1029, 944, 894, 777, 698. MS, m/z: 262 [M]$^+$. Found (%): C, 73.26; H, 8.42. Calc. for $C_{16}H_{22}O_3$ (%): C, 73.25; H, 8.45.

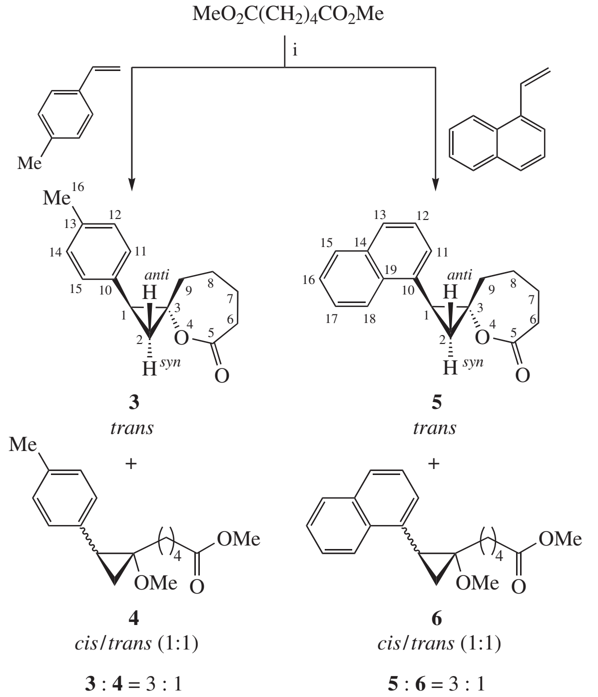
For *cis*-**2**. ^1H NMR (400 MHz, $CDCl_3$) δ: 1.01 (dd, 1H, CH_2 cyclopropane ring, ^2J 6.0 Hz, ^3J 10.0 Hz), 1.26 (t, 1H, CH_2 cyclopropane ring, J 6.5 Hz), 1.58–1.79 (m, 6H, CH_2), 1.94 (dd, 1H, CH cyclopropane ring, $^3J_{trans}$ 7.0 Hz, $^3J_{cis}$ 9.0 Hz), 2.40 (t, 2H, CH_2, J 7.4 Hz), 3.07 (s, 3H, Me), 3.70 (s, 3H, Me), 7.10–7.32 (m, 5H, Ph). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 18.87, 24.92, 25.32, 29.96, 33.65, 34.15, 51.49, 54.12, 66.46, 125.55, 127.81, 128.41, 138.28, 174.11.

For *trans*-**2**. ^1H NMR (400 MHz, $CDCl_3$) δ: 0.97 (m, 1H, CH_2 cyclopropane ring), 1.28 (m, 1H, CH_2 cyclopropane ring), 1.41–1.71 (m, 6H, CH_2), 2.20 (t, 2H, CH_2, J 7.4 Hz), 2.36 (dd, 1H, CH cyclopropane ring, $^3J_{trans}$ 7.0 Hz, $^3J_{cis}$ 9.0 Hz), 3.36 (s, 3H, Me), 3.64 (s, 3H, Me), 7.10–7.32 (m, 5H, Ph). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 17.20, 24.84, 24.92, 27.73, 29.28, 33.98, 51.40, 53.76, 66.45, 125.99, 127.86, 128.15, 138.18, 174.08.

signals of the methylene C^2H_2, the methine C^1H protons of the cyclopropane ring and the methylene protons of the lactone ring C^9H_2. The second resonance signal gave cross-peaks with the ^1H NMR multiplet signals belonging to the C^6 and C^7 methylene protons. On the basis of spectral data analysis the structure of spirolactone **1** was assigned as *cis*/*trans*-1-phenyl-4-oxaspiro-[2.6]nonan-5-one.

Under optimized conditions, 4-methylstyrene and 1-vinylnaphthalene reacted similarly giving ε-spirocyclopropyl-ε-caprolactones **3** and **5**, respectively (Scheme 2). Small amounts (20%) of substituted cyclopropanes **4** and **6** as by-products were also obtained. Unlike **1**, in this case, *trans* spirocyclopropyl lactones **3** and **5** were exclusively formed possibly due to the substituent effects, both steric and electronic, induced.[‡]

The complete analysis of spectral data deduced the structures of substituted ε-spirocyclopropyl-ε-caprolactones **3** and **5** as *trans*-1-(4-methylphenyl)-4-oxaspiro[2.6]nonan-5-one and *trans*-1-naphthyl-4-oxaspiro[2.6]nonan-5-one, respectively. The *trans*-configuration of these compounds was confirmed by the 2D NOESY NMR experiment. The obvious cross peak between the proton signal at δ 1.28 (H_aC^2) and the *ortho*-proton doublet signal at δ 7.07 ($HC^{11,15}$) in the NOESY spectrum of **3** provided evidence for the *anti*-arrangement of the tolyl moiety relative to the ester group.



Scheme 2 *Reagents and conditions*: i, $EtAlCl_2$, Mg, Cp_2ZrCl_2, THF, 20 °C, 8 h.

Similarly, the NOESY spectrum of **5** contained the cross peak between the proton signals at δ 7.21 (HC^{11}) and 1.47 (HC^2). The latter signal was attributed to proton *anti*-oriented towards the carbonyl group that based upon the value of *trans*-vicinal coupling constant $^3J(H^2_{anti} = H^1)$ 7 Hz contrary to $^3J(H^2_{syn} = H^1)$ 10 Hz.[15] The strong anisotropic naphthyl moiety in the molecule caused the essential diastereotopicity for methylene protons $\Delta\delta = \Delta[\delta(H_aC^9) - \delta(H_bC^9)] = 0.95$ ppm compared with the less anisotropic tolyl substituent $\Delta\delta = \Delta[\delta(H_aC^9) - \delta(H_bC^9)] = 0.29$ ppm in **3**. This additionally confirmed *anti*-arrangement of aryl substituents relative to the carboxyl groups in **3** and **5**.

The structure of compound **3** assigned as *trans*-1-(4-methylphenyl)-4-oxaspiro[2.6]nonan-5-one was unambiguously confirmed by X-ray diffraction analysis (Figure 1).[§] Suitable crystals

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[‡] trans-*1-(4-Methylphenyl)-4-oxaspiro[2.6]nonan-5-one* **3**. Yield 60%, mp 125–126 °C, R_f 0.59 (hexane–ethyl acetate, 1:1). IR (KBr, ν/cm^{-1}): 3435, 3022, 2939, 2861, 1908, 1740, 1516, 1433, 1292, 1193, 1149, 1014, 960, 880, 851, 818, 757, 671, 592, 528, 504. ^1H NMR (400 MHz, $CDCl_3$) δ: 1.28 (t, 1H, CH_2 cyclopropane ring, *J* 7.0 Hz), 1.45 (dd, 1H, CH_2 cyclopropane ring, ^2J 7.0 Hz, ^3J 10.0 Hz), 1.54 (m, 2H, CH_2), 1.69 (m, 1H, CH_2), 1.82 (m, 2H, CH_2), 1.83 (m, 1H, CH_2), 2.35 (s, 3H, Me), 2.64 (dd, 1H, CH cyclopropane ring, ^3J 7.0 Hz, ^3J 10.0 Hz), 2.78 (m, 2H, CH_2), 7.06–7.28 (m, 4H, Ph). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 17.49, 21.03, 22.96, 26.28, 30.12, 30.34, 35.45, 65.43, 128.13, 129.20, 133.23, 136.39, 176.44. MS, *m*/*z*: 230 [M]$^+$. Found (%): C, 77.68; H, 7.86. Calc. for $C_{15}H_{18}O_2$ (%): C, 78.23; H, 7.88.

Methyl 5-[1-methoxy-2-(4-methylphenyl)cyclopropyl]pentanoate **4**, *cis–trans* isomer mixture. Yield 18%, R_f 0.68 (hexane–ethyl acetate, 1:1). IR (KBr, ν/cm^{-1}): 3470, 2932, 2863, 1738, 1516, 1436, 1243, 1172, 1068, 821, 730. MS, *m*/*z*: 276 [M]$^+$. Found (%): C, 73.66; H, 8.72. Calc. for $C_{17}H_{24}O_3$ (%): C, 73.88; H, 8.75.

For *cis*-**4**. ^1H NMR (400 MHz, $CDCl_3$) δ: 0.97 (m, 1H, CH_2 cyclopropane ring), 1.21 (t, 1H, CH_2 cyclopropane ring, *J* 7.0 Hz), 1.43–1.78 (m, 4H, CH_2), 1.71 (m, 2H, CH_2), 1.92 (dd, 1H, CH cyclopropane ring, $^3J_{trans}$ 7.0 Hz, $^3J_{cis}$ 9.0 Hz), 2.35 (s, 3H, Me), 2.36 (m, 2H, CH_2), 3.08 (s, 3H, Me), 3.70 (s, 3H, Me), 7.04–7.28 (m, 4H, Ph). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 18.53, 20.09, 24.92, 25.32, 29.63, 33.64, 34.16, 51.47, 54.12, 66.23, 127.69, 128.85, 135.09, 135.47, 174.13.

For *trans*-**4**. ^1H NMR (400 MHz, $CDCl_3$) δ: 0.94 (m, 1H, CH_2 cyclopropane ring), 1.05 (m, 2H, CH_2), 1.25 (m, 1H, CH_2 cyclopropane ring), 1.43–1.78 (m, 4H, CH_2), 2.22 (t, 2H, CH_2, *J* 7.0 Hz), 2.33 (m, 1H, CH cyclopropane ring), 2.35 (s, 3H, Me), 3.36 (s, 3H, Me), 3.67 (s, 3H, Me), 7.04–7.28 (m, 4H, Ph). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 17.19, 20.09, 24.84, 24.89, 27.74, 28.85, 34.02, 51.39, 53.73, 66.52, 128.29, 128.60, 134.99, 135.47, 174.13.

trans-*1-Napthyl-4-oxaspiro[2.6]nonan-5-one* **5**. Yield 60%, R_f 0.49 (hexane–ethyl acetate, 1:1). IR (KBr, ν/cm^{-1}): 3435, 3048, 2929, 2861, 1738, 1620, 1596, 1509, 1434, 1237, 1197, 1150, 1079, 1043, 1020, 975, 859, 802, 547, 516. ^1H NMR (400 MHz, $CDCl_3$) δ: 0.95 (m, 1H, CH_2), 1.47 (dd, 1H, CH_2 cyclopropane ring, ^2J 7.0 Hz, ^3J 10.0 Hz), 1.52 (m, 1H, CH_2), 1.62 (m, 1H, CH_2), 1.65 (m, 1H, CH_2 cyclopropane ring), 1.72 (m, 1H, CH_2), 1.83 (m, 1H, CH_2), 1.96 (m, 1H, CH_2), 2.82 (m, 2H, CH_2), 3.09 (dd, 1H, CH cyclopropane ring, ^3J 7.0 Hz, ^3J 10.0 Hz), 7.07–8.31 (m, 7H, arom.). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 16.95, 23.11, 27.07, 29.09, 29.79, 37.77, 65.71, [124.76, 125.34, 125.38, 126.18, 126.56, 127.76, 128.40, 133.41, 133.48, 133.68 (arom.)], 176.63. MS, *m*/*z*: 266 [M]$^+$. Found (%): C, 80.92; H, 6.84. Calc. for $C_{18}H_{18}O_2$ (%): C, 81.17; H, 6.81.

Methyl 5-[1-methoxy-2-(1-napthyl)cyclopropyl]pentanoate **6**, *cis–trans* isomer mixture. Yield 15%, R_f 0.69 (hexane–ethyl acetate, 1:1). IR (KBr, ν/cm^{-1}): 3448, 3047, 2945, 2867, 2826, 1737, 1595, 1508, 1456, 1436, 1401, 1364, 1317, 1242, 1172, 1073, 1017, 801, 779, 736. MS, *m*/*z*: 312 [M]$^+$. Found (%): C, 76.35; H, 7.64. Calc. for $C_{20}H_{24}O_3$ (%): C, 76.89; H, 7.74.

For *cis*-**6**. ^1H NMR (400 MHz, $CDCl_3$) δ: 0.97 (m, 1H, CH_2 cyclopropane ring), 1.20 (m, 1H, CH_2 cyclopropane ring), 1.49–1.85 (m, 4H, CH_2), 1.69 (m, 2H, CH_2), 2.04 (m, 1H, CH cyclopropane ring), 2.41–2.46 (m, 2H, CH_2), 3.50 (s, 3H, Me), 3.72 (s, 3H, Me), 7.28–8.37 (m, 7H, arom.). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 16.85, 24.98, 25.41, 28.42, 33.96, 34.01, 51.53, 54.04, 66.38, [124.15, 124.55, 124.65, 124.99, 125.32, 125.40, 125.70, 125.77, 125.84, 126.57, 126.97, 128.52, 128.67, 128.87, 133.56, 133.71, 134.68 arom. (*cis*/*trans*)], 174.12.

For *trans*-**6**. ^1H NMR (400 MHz, $CDCl_3$) δ: 0.95 (m, 1H, CH_2 cyclopropane ring), 1.25 (m, 1H, CH_2 cyclopropane ring), 1.11 (m, 2H, CH_2), 1.49–1.85 (m, 4H, CH_2), 2.36 (m, 1H, CH cyclopropane ring), 2.41–2.46 (m, 2H, CH_2), 3.57 (s, 3H, Me), 3.65 (s, 3H, Me), 7.28–8.37 (m, 7H, arom.). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 16.24, 24.41, 24.80, 27.30, 27.86, 33.79, 51.34, 53.85, 66.98, [124.15, 124.55, 124.65, 124.99, 125.32, 125.40, 125.70, 125.77, 125.84, 126.57, 126.97, 128.52, 128.67, 128.87, 133.56, 133.71, 134.68 arom. (*cis*/*trans*)], 173.98.

[§] *Crystal data for* trans-**3**. Crystal of $C_{15}H_{18}O_2$ ($M = 230.29$) is colourless, crystal dimensions 0.7×0.3×0.2 mm, triclinic, space group $P\bar{1}$ (no. 2), at 170(2) K: $a = 6.6681(10)$, $b = 7.3872(9)$ and $c = 13.103(2)$ Å, $\alpha = 76.966(12)°$, $\beta = 79.628(13)°$, $\gamma = 79.063(12)°$, $V = 610.99(15)$ Å^3, $d_{calc} = 1.252$ g cm^{-3}, $Z = 2$, μ(MoKα) = 0.081 mm^{-1}; 10525 reflections measured, 3602 unique reflections ($R_{int} = 0.0399$), $F(000) = 248$, $5.74 < 2\theta < 62.28°$, 226 parameters were used in calculations, GOF = 0.981, final *R* indexes [$I > 2\sigma(I)$]: $R_1 = 0.0502$, $wR_2 = 0.1208$; *R* indexes (all data): $R_1 = 0.0762$, $wR_2 = 0.1311$.

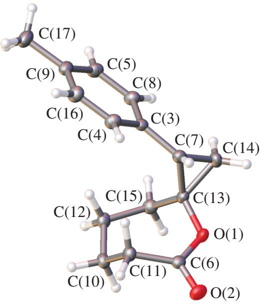
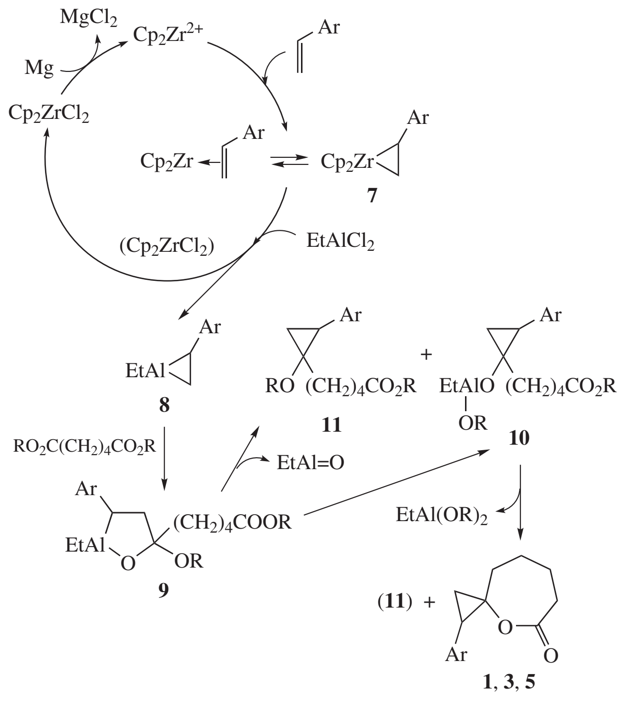


Figure 1 X-ray crystallographic structure of **3**.

of **3** for X-ray crystallographic study have been grown from chloroform.

The molecular structure of **3** is composed of the *p*-tolyl and spirocyclopropyl lactone units (see Figure 1). The spirocyclopropyl lactone fragment upon cyclization adopted the configuration of a beveled chair. *trans*-Orientation of the *p*-tolyl substituent relative to the ester group combined in the seven-membered lactone ring is described by dihedral angle C(3)C(7)C(13)O(1) equal to 145.08°.

Our experimental findings allowed us to propose possible ways for the formation of ε-spirocyclopropyl-ε-capralactones (Scheme 3). We hypothesized that at the first stage the generation of coordinatively unsaturated complex Cp_2Zr^{2+} occurs *via* Mg-reduction of Cp_2ZrCl_2 giving 2-aryl-substituted zirconacyclopropane **7** in the presence of vinylarene. The latter reacts with $EtAlCl_2$ to yield aluminacyclopropane **8**. The interaction between **8** and diester affords labile oxaaluminacyclopentane **9**, which can undergo further intramolecular rearrangement to cyclopropane intermediate **10** and **11** as a minor product. Subsequent intramolecular rearrangement of **10**, which is accompanied by elimination of $EtAl(OR)_2$, favors the ring closure thus providing formation of the ε-spirocyclopropyl-ε-lactone molecule **1**, **3** or **5**.



Scheme 3

Further observations have shown that diesters having distances between the ester groups of less or more than four CH_2 units do not contribute to the formation of substituted spirolactones. In this case, the corresponding substituted cyclopropanes of type **11** are the end products, being in good agreement with the scheme of the reaction mechanism proposed previously.[14] Apparently, in the case of dimethyl adipate, the reaction has somewhat different mechanism to give the intermediate **10**. The transformation of the latter can explain the formation of the end spirolactones **1**, **3**, and **5**.

In conclusion, we have elaborated a new one-pot method for the synthesis of ε-spirocyclopropyl-ε-caprolactones in 60% yield *via* the reaction of vinylarenes with $EtAlCl_2$ and dimethyl adipate catalyzed by Cp_2ZrCl_2 (10 mol%). The reaction with 4-methylstyrene and 1-vinylnaphthalene exclusively affords *trans*-configurated ε-spirocyclopropyl-ε-caprolactones. Only one ester group participates in the reaction, while the other one remains untouched.

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X-ray data were collected on an Xcalibur Eos diffractometer equipped with imaging plate detector using graphite-monochromated MoKα radiation (λ = 0.71073 Å). Using Olex2,[16] the crystal structure was solved with the SHELXS[17] structure solution program using Direct Methods and refined with SHELXL[17] refinement package using Least Squares minimization. The crystal was anchored on a matrix with silicon grease to prevent the possibility of decay of the crystal during data collection.

CCDC 911326 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2014.