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Reaction of Methyl 1-Bromocyclopentanecarboxylate with Zinc and 1-Aryl-5-phenylpenta-1,4-dien-3-ones

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Abstract—Methyl 1-bromocyclopentanecarboxylate reacted with zinc and 1-aryl-5-phenylpenta-1,4-dien-3-ones with the formation of isomeric 10-aryl-8-(2-arylethenyl)-7-oxaspiro[4.5]dec-8-en-6-ones.

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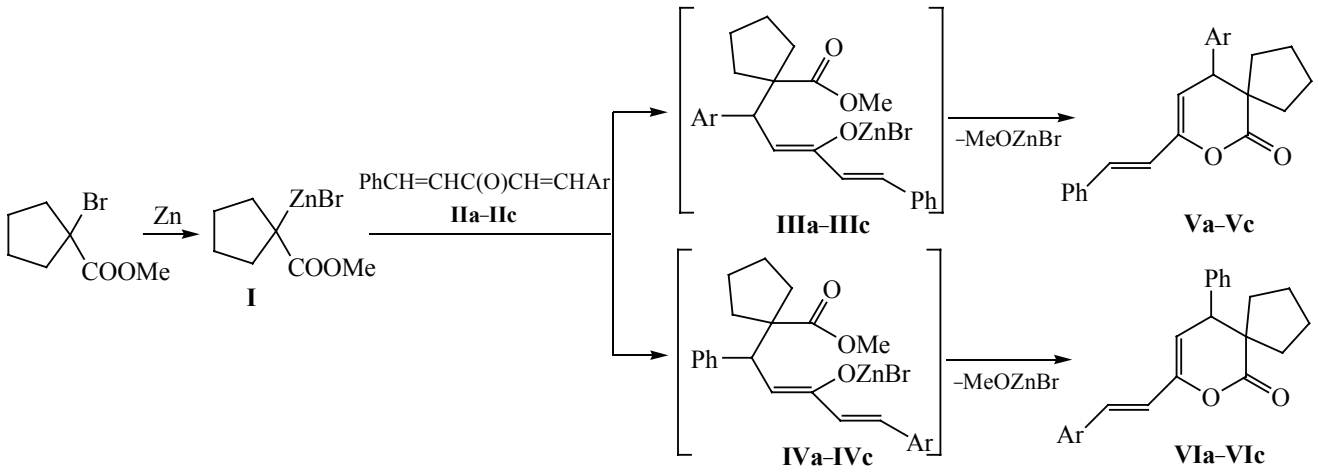
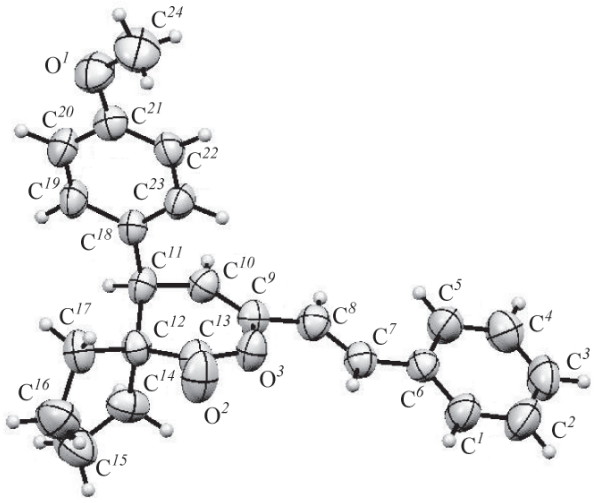
It has been formerly established that the acyclic Reformatsky reagents react with symmetric 1,5-diarylpenta-1,4-dien-3-ones giving spiro-3,4-dihydropyran-2-ones with an aryl substituent in the position *4* and an arylethenyl substituent in the position *6* of the heterocycle [1]. In the case of different aryl substituents in the 1,5-diarylpenta-1,4-dien-3-ones presumably two structural isomers may form. Actually, as showed our studies, the reaction of Reformatsky reagent **I** obtained from methyl 1-bromocyclopentanecarboxylate and zinc with 1-(4-methoxyphenyl)-5-phenylpenta-1,4-dien-3-one (**IIa**) afforded 10-(4-methoxyphenyl)-8-(2-phenylethenyl)-7-oxaspiro[4.5]dec-8-en-6-one (**Va**) in 22% yield and 8-[2-(4-methoxyphenyl)ethenyl]-10-phenyl-7-oxaspiro[4.5]dec-8-en-6-one (**VIa**) in 26% yield arising as a result of the 1,4-addition of the organozinc compound to one of the C=C–C=O fragments of the dienone forming intermediates **IIIa, IVa** followed by their cyclization with the liberation of zinc bromomethylate.

The composition and structure of compounds **Va, VIa** were confirmed by the data of elemental analysis, IR, ^{1}H NMR, and mass spectra. The structure of compound **Va** was proved by XRD analysis.



Ar = 4-MeOC$_6$H$_4$ (**a**), 4-ClC$_6$H$_4$ (**b**), 4-BrC$_6$H$_4$ (**c**).

According to XRD data the compound crystallizes in a chiral space group of symmetry in a rhombic crystal system. The general view of the molecule is given on the figure. The structure is characterized by the *S-trans*-configuration of the butadiene fragment and *trans*-configuration of the ethylene fragment C^7–C^8. The bond lengths and bond angles are close to the standard values. The phenyl substituent as a whole lies in the plane of the conjugated butadiene system. The dihydropyranone ring is nonplanar and has a structure of a sheet folded along the axis going through atoms C^9–C^{12}. The angle between the least-mean-square planes $C^{13}C^{12}O^3C^9$ and $C^9C^{10}C^{11}C^{12}$ equals 32.7 deg. The methoxyphenyl substituent is located in a pseudoaxial position. The atom C^{15} of the cyclopentane ring is disordered in the position *2* with the population factors 0.5. The crystal packing lacks any pronounced shortened contacts.



Geometry of compound **Va** according to XRD analysis presented in ellipsoids of 50% probablility.

The reaction of Reformatsky reagent **I** with dienones **IIb, IIc** led to the formation of virtually individual reaction products. According to the chromatography the content of the minor products in the separated mixtures was 6.2 and 1.5% respectively. Inasmuch as in the ^{1}H NMR spectra of compounds obtained the chemical shifts of the proton signals of the ethenyl groups (6.49 and 7.12 ppm) coincide with the chemical shifts of protons of this group in compound **Va** (6.49 and 7.11 ppm) (proton signals of the ethenyl group of compound **VIa** are observed at 6.37 and 7.07 ppm), a conclusion is logical that in all these compound the phenyl substituent is attached to its group, and the main reaction products are compound **Vb, Vc**.

The same conclusion follows from the analysis of mass spectra. The mass spectra of compounds **Va, VIa** contain the same peaks, but the pronounced difference in intensity exists for cations with the values of *m/z* 161 $[ArCH{=}CHCO]^+$, 133 $[ArCH{=}CH]^+$, 131 $[PhCH{=}CHCO]^+$, 103 $[PhCH{=}CH]^+$. This difference shows firstly that the fragmentation character is governed mainly by the identical part of the isomers structure, Secondly, the triple increase (from 6/17 to 10/9) in the ratio of the intensity of the signal of ion $[ArCH{=}CH]^+$ to that of the ion $[PhCH{=}CH]^+$ in going from **Va** to **VIa** indicates independently of XRD data that the first compound has **V** structure, and the second one, **VI** structure, since it is expectable to obtain the arylvinyl ion predominantly from the substituent in the position *8*. In the mass spectra of the halosubstituted compounds the intensity of peaks of ions $[PhCH{=}CHCO]^+$ and $[PhCH{=}CH]^+$ in the predominant isomers is higer than the intensity of peaks of ions $[ArCH{=}CHCO]^+$ and $[ArCH{=}CH]^+$, whereas in the spectra of the minor isomers the intensity of the former peaks sharply decreases and of the latter peaks significantly grows. This means that the characteristic region of spectra of the prevailing isomers is qualitatively similar to the spectrum of compound **Va**, and the spectra of the minor isomers resemble that of compound **VIa**. Therefore in keeping with the mass spectral data the prevailing isomers of the chloro- and bromo-substituted compounds should be identified as structures **Vb, Vc**.

EXPERIMENTAL

IR spectra were recorded on a spectrophotometer Specord 75IR from mulls in mineral oil. ^{1}H NMR spectra were registered on a spectrometer Mercury Plus-300 (300 MHz) from solutions in $CDCl_3$, internal reference HMDS. Chromatograms and mass spectra were obtained on a GC-MS instrument Agilent 6890N/5975B (column HP-5ms, 30 m × 0.25 mm × 0.25 μm, carrier gas helium, ionization by electron impact, 70 eV).

XRD analysis of compound **Va** was carried out on an automatic four-circle diffractometer Xcalibur 3 with a CCD-detector along a standard procedure [*T* 295(2) K, MoK_α-radiation, graphite monochromator, ω-scanning, scanning step 1°]. No correction for extinction was done (μ 0.080 mm^{-1}). Crystal rhombic, space group $P2_12_12_1$, *a* 6.1724(4), *b* 17.0843(18), *c* 18.357(2) Å, *V* 1935.8(3) Å^3. $C_{24}H_{24}O_3$. *Z* 4. Within scattering angles $2.63 < \theta < 26.39°$ 11046 reflections were collected, among them 2295 independent (R_{int} 0.0475), 1052 with

$I > 2\sigma(I)$, completeness 99.7%. The structure was solved by the direct method and refined using program package SHELXTL-97 [2] in the anisotropic (isotropic for hydrogen atoms) approximation. Some hydrogen atoms were solved directly and refined independently, a part of hydrogen atoms was located in the geometrically calculated positions and was included in refining in the *rider* model with dependent thermal parameters. The final refinement parameters: R_1 0.0321, wR_2 0.0508 [$I > 2\sigma(I)$], R_1 0.0895, wR_2 0.0542 (with respect to all reflections) at quality factor 1.000. The peaks of maximum and minimum residual electron density are 0.106 and –0.109 ē Å^{-3}.

The complete set of the crystallographic data of compound **Va** is deposited in the Gambridge Crystallographic Database (CCDC no. 893372) and is available at the address www.ccdc.cam.ac.uk/conts/retrieving.html (or CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Compounds Va–Vc, VIa. General procedure. A mixture of 1.5 g of fine zinc turnings, a catalytic quantity of mercury(II) chloride, 5 mmol of 1-aryl-5-phenyl-penta-1,4-dien-3-one, 5.1 mmol of methyl 1-bromocyclopentanecarboxylate, 20 ml of benzene, 5 ml of ethyl acetate, and 1 ml of HMPA was boiled for 2 h, cooled, decanted from excess zinc, and was treated with 5% solution of hydrochloric acid. The organic layer was separated, the water layer was twice extracted with ethyl actate. The organic solutions were dried with anhydrous sodium sulfate, the solvent was distilled off, the reaction products were recrystallized from ethyl acetate.

10-(4-Methoxyphenyl)-8-(2-phenylethenyl)-7-oxaspiro[4.5]dec-8-en-6-one (Va). Yield 0.40 g (22%), mp 164–165°C. IR spectrum, ν, cm^{-1}: 1765 (C=O), 1660 (C=C). ^{1}H NMR spectrum, δ, ppm: 1.32–2.10 m [8H, $(CH_2)_4$], 3.32 d (1H, H^{10}, *J* 6.3 Hz), 3.77 s (3H, OMe), 5.52 d (1H, H^9, *J* 6.3 Hz), 6.49 d, 7.11 d (2H, CH=CH, *J* 15.9 Hz), 6.81 d, 7.03 d (4H, 4-MeOC$_6$H$_4$, *J* 8.7 Hz), 7.26 d, 7.33 t, 7.44 d (5H, Ph, *J* 7.8 Hz). Mass spectrum, *m/z* (I_{rel}, %): 360 [*M*]$^+$ (39), 265 [*M* – C_5H_7CO]$^+$ (55), 264 [*M* – C_5H_8CO]$^+$ (100), 263 [*M* – C_5H_9CO]$^+$ (32), 161 [$CH_3OC_6H_4CH$=CHCO]$^+$ (10), 133 [$CH_3OC_6H_4CH$=CH]$^+$ (6), 131 [PhCH=CHCO]$^+$ (23), 103 [PhCH=CH]$^+$ (17), 96 [C_5H_8CO]$^+$ (4), 77 [Ph]$^+$ (12), 68 [C_5H_8]$^+$ (7). Found, %: C 80.09; H 6.92. $C_{24}H_{24}O_3$. Calculated, %: C 79.97; H 6.71.

8-(2-Phenylethenyl)-10-(4-chlorophenyl)-7-oxaspiro[4.5]dec-8-en-6-one (Vb). Yield 0.77 g (42%), mp 182–184°C. IR spectrum, ν, cm^{-1}: 1770 (C=O), 1655 (C=C). ^{1}H NMR spectrum, δ, ppm: 1.08–2.13 m [8H, $(CH_2)_4$], 3.34 d (1H, H^{10}, *J* 6.6 Hz), 5.50 d (1H, H^9, *J* 6.6 Hz), 6.49 d, 7.12 d (2H, CH=CH, *J* 15.6 Hz), 7.05 d, 7.25 d (4H, 4-ClC$_6$H$_4$, *J* 8.4 Hz), 7.28 d [1H, C^n (Ph), *J* 7.5 Hz], 7.34 t [2H, Cm (Ph), *J* 7.5 Hz], 7.44 d [2H, C^o (Ph), *J* 7.5 Hz]. Mass spectrum, *m/z* (I_{rel}, %): 364 [*M*]$^+$ (24), 269 [*M* – C_5H_7CO]$^+$ (100), 268 [*M* – – C_5H_8CO]$^+$ (4), 267 [*M* – C_5H_9CO]$^+$ (8), 165 [ClC_6H_4CH=CHCO]$^+$ (5), 137 [ClC_6H_4CH=CH]$^+$ (2), 131 [PhCH=CHCO]$^+$ (36), 103 [PhCH=CH]$^+$ (18), 96 [C_5H_8CO]$^+$ (56), 77 [Ph]$^+$ (12), 68 [C_5H_8]$^+$ (22). Found, %: C 75.82; H 5.92; Cl 9.60. $C_{23}H_{21}ClO_2$. Calculated, %: C 75.71; H 5.80; Cl 9.72.

10-(4-Bromophenyl)-8-(2-phenylethenyl)-7-oxaspiro[4.5]dec-8-en-6-one (Vc). Yield 0.92 g (45%), mp 204–206°C. IR spectrum, ν, cm^{-1}: 1770 (C=O), 1655 (C=C). ^{1}H NMR spectrum, δ, ppm: 1.10–2.12 m [8H, $(CH_2)_4$], 3.33 d (1H, H^{10}, *J* 6.6 Hz), 5.49 d (1H, H^9, *J* 6.6 Hz), 6.49 d, 7.12 d (2H, CH=CH, *J* 15.9 Hz), 6.99 d, 7.41 d (4H, 4-BrC$_6$H$_4$, *J* 8.4 Hz), 7.28 d, 7.34 t, 7.44 d (5H, Ph, *J* 7.5 Hz). Mass spectrum, *m/z* (I_{rel}, %): 408 [*M*]$^+$ (17), 313 [*M* – C_5H_7CO]$^+$ (83), 312 [*M* – C_5H_8CO]$^+$ (3), 311 [*M* – C_5H_9CO]$^+$ (7), 209 [BrC_6H_4CH=CHCO]$^+$ (3), 181 [BrC_6H_4CH=CH]$^+$ (3), 131 [PhCH=CHCO]$^+$ (61), 103 [PhCH=CH]$^+$ (36), 96 [C_5H_8CO]$^+$ (100), 77 [Ph]$^+$ (26), 68 [C_5H_8]$^+$ (46). Found, %: C 67.61; H 5.11; Br 19.33. $C_{23}H_{21}BrO_2$. Calculated, %: C 67.49; H 5.17; Br 19.52.

8-[2-(4-Methoxyphenyl)ethenyl]-10-phenyl-7-oxaspiro[4.5]dec-8-en-6-one (VIa). Yield 0.47 g (26%), mp 123–124°C. IR spectrum, ν, cm^{-1}: 1765 (C=O), 1665 (C=C). ^{1}H NMR spectrum, δ, ppm: 1.32–2.12 m [8H, $(CH_2)_4$], 3.35 d (1H, H^{10}, *J* 6.3 Hz), 3.81 s (3H, OMe), 5.48 d (1H, H^9, *J* 6.3 Hz), 6.37 d, 7.07 d (2H, CH=CH, *J* 15.9 Hz), 6.87 d, 7.38 d (4H, 4-MeOC$_6$H$_4$, *J* 8.7 Hz), 7.22–7.32 m (5H, Ph). Mass spectrum, *m/z* (I_{rel}, %): 360 [*M*]$^+$ (48), 265 [*M* – C_5H_7CO]$^+$ (54), 264 [*M* – C_5H_8CO]$^+$ (100), 263 [*M* – C_5H_9CO]$^+$ (32), 161 [$CH_3OC_6H_4CH$=CHCO]$^+$ (40), 133 [$CH_3OC_6H_4CH$=CH]$^+$ (10), 131 [PhCH=CHCO]$^+$ (5), 103 [PhCH=CH]$^+$ (9), 96 [C_5H_8CO]$^+$ (4), 77 [Ph]$^+$ (8), 68 [C_5H_8]$^+$ (6). Found, %: C 79.82; H 6.84. $C_{24}H_{24}O_3$. Calculated, %: C 79.97; H 6.71.

10-Phenyl-8-[2-(4-chlorophenyl)ethenyl]-7-oxaspiro[4.5]dec-8-en-6-one (VIb). Mass spectrum, *m/z* (I_{rel}, %): 364 [*M*]$^+$ (27), 269 [*M* – C_5H_7CO]$^+$ (100), 268 [*M* – C_5H_8CO]$^+$ (4), 267 [*M* – C_5H_9CO]$^+$ (8), 165

$[ClC_6H_4CH=CHCO]^+$ (28), 137 $[ClC_6H_4CH=CH]^+$ (6), 131 $[PhCH=CHCO]^+$ (3), 103 $[PhCH=CH]^+$ (8), 96 $[C_5H_8CO]^+$ (59), 77 $[Ph]^+$ (7), 68 $[C_5H_8]^+$ (22).

8-[2-(4-Bromophenyl)ethenyl]-10-phenyl-7-oxaspiro[4.5]dec-8-en-6-one (VIc). Mass spectrum, *m/z* (I_{rel}, %): 408 $[M]^+$ (20), 313 $[M - C_5H_7CO]^+$ (91), 312 $[M - C_5H_8CO]^+$ (4), 311 $[M - C_5H_9CO]^+$ (9), 209 $[BrC_6H_4CH=CHCO]^+$ (21), 181 $[BrC_6H_4CH=CH]^+$ (4), 131 $[PhCH=CHCO]^+$ (17), 103 $[PhCH=CH]^+$ (23), 96 $[C_5H_8CO]^+$ (100), 77 $[Ph]^+$ (16), 68 $[C_5H_8]^+$ (43).

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