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Investigation of Reactions of the Organozinc Reagents Prepared from Zinc and Dialkyl Dibromomalonates with the Derivatives of 2-Arylmethyleneindan-1,3-dione and 5-Arylmethylene-2,2-dimethyl-1,3-dioxane-4,6-dione

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Abstract—Organozinc compounds prepared from dialkyl dibromomalonates and zinc react with 2-arylmethyleneindan-4,6-diones, 5-arylmethylene-2,2-dimethyl-1,3-dioxane-4,6-diones, as well as with 2-[4-(1,3-dioxoindan-2-ylidenemethyl)phenyl]methyleneindan-1,3-dione and 5-[4-(2,2-dimethyl-4,6-dioxo-1,3-dioxane-2-ylidenemethyl)phenyl]methylene-2,2-dimethyl-1,3-dioxane-4,6-diones to form dialkyl 3-aryl-1'3'-dioxaspiro(cyclopropane-2,2'-indan)-1,1-dicarboxylates, dimethyl 3-aryl-6,6-dimethyl-5,7-dioxa-4,8-dioxaspiro[2,5]octan-2,2-dicarboxylates, dialkyl 2-{4-[3,3-bis (alkoxycarbonyl)-1',3'-dioxaspiro(cyclopropane-2,2'-indan)-1-yl]phenyl}-1',3'-dioxaspiro[cyclopropane-2,2'-indan]-1,1-dicarboxylates, and dialkyl 2-{4-[2,2-bis(alkoxycarbonyl)-6,6'-dimethyl-4,8-dioxo-5,7-dioxaspiro[2,5]oct-1-yl]phenyl}-6,6-dimethyl-4,8-dioxo-5,7-dioxaspiro[2,5]octan-1,1-dicarboxylate respectively.

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The organozinc reagents prepared from dialkyl dibromomalonates were used prevoiusly for cyclopropanation of dialkyl alkylidenemalonates [1], 3-aryl-2-cyanopropenoic acid, and 2-arylmethylenemalonic acid dinitriles [2], and also for cyclopropanation of primary amides of 3-aryl-2-cyanopropenoic acid [3].

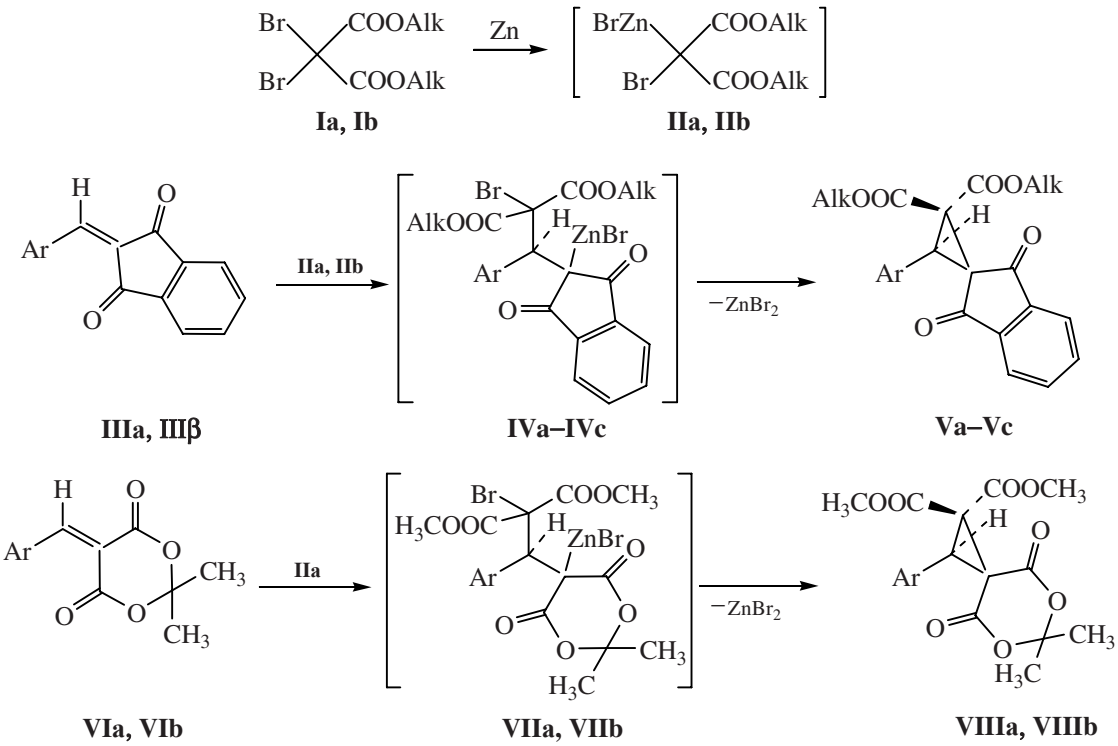
In this study aiming to obtain cyclopropane derivatives having two geminal alkoxycarbonyl groups and also a spiro carbon atom we investigated the reaction of organozinc compounds **IIa** and **IIb** formed from dialkyl dibromomalonates **Ia, Ib** and zinc with 2-arylmethyleneindan-1,3-diones **IIIa, IIIb** and 5-arylmethylene-2,2-dimethyl-1,3-dioxan-4,6-diones **Ia, VIb**. It was found that the reaction actually yielded the cyclopropanation products according to Scheme 1.

Organozinc compounds **IIa, IIb** prepared preliminary from dibromoesters **Ia, Ib** and zinc in the ether–THF–toluene medium add to the double bond of electrophilic substrates **IIIa, IIIb**, **VIa**, and **VIb** to form the intermediates **IVa–IVc, VIIa**, and **VIIb** that under the reaction conditions undergo cyclization to give the target products, dialkyl 3-aryl-1',3'-dioxospiro [cyclopropane-2,2'-indan]-1,1-dicarboxylates **Va–Vc** and dimethyl 3-aryl-6,6-dimethyl-5,7-dioxa-4,8-dioxospiro[2.5] octane-2,2-dicarboxylates **VIIIa, VIIIb** respectively.

The composition and structure of compounds **Va–Vc, VIIIa,** and **VIIIb** were confirmed by the elemental analysis and IR and ^{1}H NMR spectra. In the IR spectra of compounds **Va–Vc** the characteristic absorption bands (ν, cm^{-1}) of ketones (1690–1695) and esters (1720–1725) are observed. The ^{1}H NMR spectra of these compounds contain the characteristic signals at δ 4.05–4.20 ppm corresponding to the methine proton (CH), and also the signals of methoxy groups at δ 3.78–3.84 ppm (compounds **Va, Vc**) and of ethoxy groups at δ 1.17–1.31 ppm and 4.18–4.31 ppm (compound **Vb**). In the IR spectra of compounds **VIIIa, VIIIb** the characteristic bands of the ester and lactone carbonyls at 1720 and 1745 cm^{-1} are observed. The ^{1}H NMR spectra of compounds **VIIIa, VIIIb** contain the signals at 4.21–4.37 ppm belonging to the methine proton, the signals of two methoxy groups at 3.70–3.80 ppm and 3.79–3.87 ppm, and also the signals of two methyl substituents in the dioxane ring at 1.79–1.85 and 1.99–2.06 ppm.

† Deceased.

Scheme 1.



I, II, Alk = CH_3 (**a**), CH_3CH_2 (**b**); **III**, Ar = Ph (**a**), 4-BrC_6H_4 (**b**); **IV–V**, Ar = C_6H_5, Alk = CH_3 (**a**), CH_3CH_2 (**b**), Ar = 4-BrC_6H_4, Alk = CH_3 (**c**); **VI–VIII**, Ar = 4-BrC_6H_4 (**a**), 3-$NO_2C_6H_4$ (**b**).

Reaction of organozinc derivatives **IIa, IIb** with 2-[4-(1,3-dioxoindan-2-ylidenemethyl)phenyl] methyleneindan-1,3-dione **IX** and 5-[4-(2,2-dimethyl-4,6-dioxo-1,3-dioxan-2-ylidenemethyl)phenyl]methylene-2,2-dimethyl-1,3-dioxane-4,6-dione **X** proceeds analogously leading to the corresponding cyclopropaneation products, compounds **XIa, XIb, XIIa**, and **XIIb** apparently according to Scheme 2.

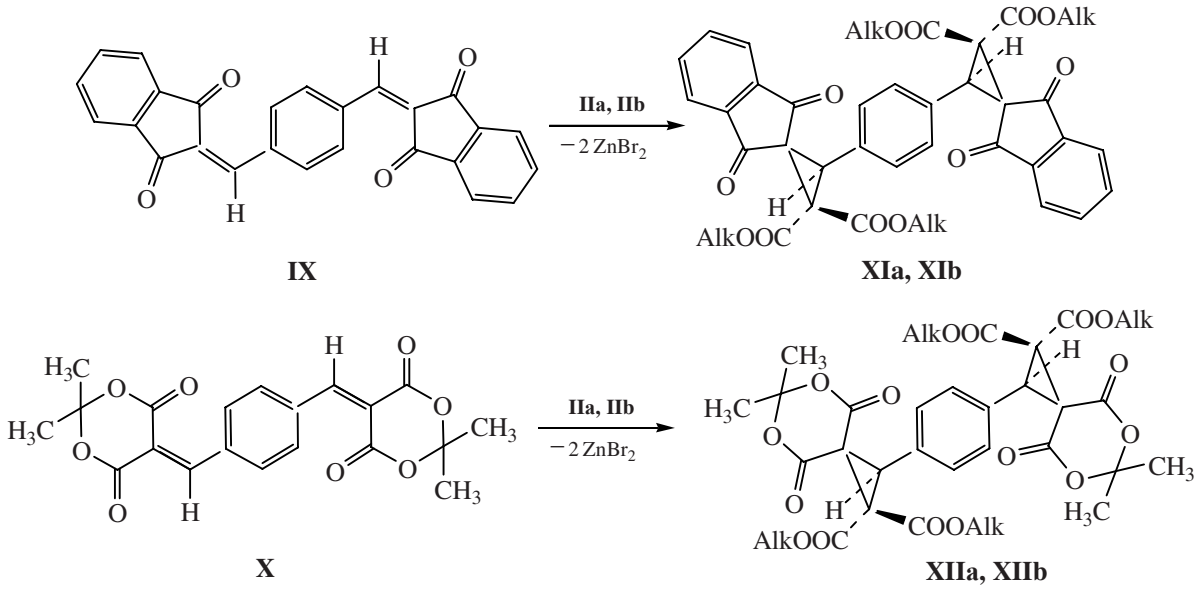
The composition and structure of compounds **XIa, XIb**, **XIIa**, and **XIIb** were confirmed by the elemental analysis and the IR and ^{1}H NMR spectra. In the IR spectra of compounds **XIa, XIb** the characteristic absorption bands from the ester and the lactone carbonyls (1700–1745 cm^{-1}) are present. The ^{1}H NMR spectra of compounds **XIa, XIb** contain a singlet at 3.89–4.04 ppm of two methine protons, and the signals of methoxy groups at 3.60 and 3.69 ppm (compound **XIa**) and of ethoxy groups at 1.15–1.30 ppm and 4.05-4.25 ppm (compound **XIb**). In the IR spectra of compounds **XIIa, XIIb** the absorption bands of keto group (1720 cm^{-1}) and the ester carbonyl (1735–1740 cm^{-1}) are present. The ^{1}H NMR spectra of compounds **XIIa, XIIb** contain the characteristic signals at 4.03–4.04 ppm attributed to the methine protons, the signals of four methyl groups from two dioxane rings at 1.75 and 1.92 ppm, and also the signals of four methoxy groups at 3.67 and 3.70 ppm (compound **XIIa**) or four ethoxy ones at 1.17 ppm and 4.18 ppm (compound **XIIb**).

EXPERIMENTAL

The IR spectra were registered on a Specord IR-75 spectrometer for the individual compounds in mineral oil. The ^{1}H NMR spectra were taken on a Tesla BS-567A (100 MHz) spectrometer in $CDCl_3$ for compound **VIIIa**, and in DMSO-d_6 for compounds **Xa, Xb, XIIa**, and **XIIb**, internal reference HMDS. The ^{1}H NMR spectra of compounds **Va–Vc** and **VIIIb** were taken on a MERCURY-Plus 300 (300 MHz) spectrometer in $CDCl_3$, internal reference HMDS.

Dialkyl 3-aryl-1',3'-dioxospiro[cyclopropane-2,2'-indan]-1,1-dicarboxylates (Va–Vc). A mixture of 2 g of fine zinc turnings, 7 ml of ether, and 14 ml of THF was treated with 0.065 mol of dialkyl dibromo-

Scheme 2.



XI, XII, Alk = CH_3 (**a**), CH_3CH_2 (**b**).

malonate. The mixture obtained was heated until the beginning of the reaction, and then the spontaneous process took place. After the completion of the reaction the mixture obtained was refluxed for 15–20 min, cooled, and decanted to another flask. Then the organic phase was treated with 0.05 mol of substrate **IIIa, IIIb** dissolved in 2 ml of THF and 10 ml of anhydrous toluene. The mixture obtained was refluxed for 50–60 min, cooled, hydrolyzed with 5% acetic acid and extracted with benzene. The extract was dried with Na_2SO_4, solvents were distilled off, and the residue crystallized from ethyl acetate–acetone mixture.

Dimethyl 3-phenyl-1',3'-dioxospiro[cyclopropane-2,2'-indan]-1,1-dicarboxylate (Va). Yield 47%, mp 128–130°C. IR spectrum (mineral oil), ν, cm^{-1}: 1690, 1725. ^1H NMR spectrum, δ, ppm: 3.72 s (3H, $COOCH_3$), 3.85 s (3H, $COOCH_3$), 4.14 s (1H, CH), 7.28–7.29 m (5H, C_6H_5), 7.85–7.86 m (4H, C_6H_4). Found, %: C 69.02; H 4.22. $C_{21}H_{16}O_6$. Calculated, %: C 69.23; H 4.43.

Diethyl 3-phenyl-1'3'-dioxospiro[cyclopropane-2,2'-indan]-1,1'-dicarboxylate (Vb). Yield 44%, mp 109–111°C. IR spectrum (mineral oil), ν, cm^{-1}: 1695, 1720. ^1H NMR spectrum, δ, ppm: 1.17 t, 1.31 t (6H, CH_3-ethyl, *J* 7.4 Hz), 4.20 s (1H, CH), 4.18 q, 4.31 q (4H, CH_2OOC, *J* 7.4 Hz), 7.25–7.31 m (5H, C_6H_5), 7.82–7.85 m (4H, C_6H_4). Found, %: C 70.19; H 4.93. $C_{23}H_{20}O_6$. Calculated, %: C 70.40; H 5.14.

Dimethyl 3-(4-bromophenyl)-1',3'-dioxospiro[cyclopropane-2,2'-indan]-1,1-dicarboxylate (Vc). Yield 40%, mp 166–168°C. IR spectrum (mineral oil), ν, cm^{-1}: 1695, 1725. ^1H NMR spectrum, δ, ppm: 3.72 s (3H, $COOCH_3$), 3.84 s (3H, $COOCH_3$), 4.05 s (1H, CH), 7.17–7.42 m (4H, 4-BrC_6H_4), 7.85–7.88 m (4H, C_6H_4). Found, %: C 55.49; H 3.20. $C_{21}H_{15}BrO_6$. Calculated, %: C 56.90; H 3.41.

Dimethyl 3-aryl-6,6-dimethyl-5,7-dioxa-4,8-dioxospiro[2.5]octan-2,2-dicarboxylates (VIIIa, IIb). These compounds were prepared by procedure similar to the above-described one. The only exclusion was that 2 ml of HMPA was added to the reaction mixture with the substrates **VIa, VIb**. The products were crystallized from methanol.

Dimethyl 3-(4-bromophenyl)-6,6-dimethyl-5,7-dioxa-4,8-dioxospiro[2.5]octane-2,2-dicarboxylate (VIIIa). Yield 46%, mp 130–132°C. IR spectrum (mineral oil), ν, cm^{-1}: 1720, 1745. ^1H NMR spectrum, δ, ppm: 1.79 s (2H, CH_3), 1.99 s (3H, CH_3), 3.70 s (3H, $COOCH_3$), 3.79 s (3H, $COOCH_3$), 4.21 s (1H, CH), 7.09–7.39 m (4H, 4-BrC_6H_4). Found, %: C 48.79; H 2.67. $C_{18}H_{17}BrO_8$. Calculated, %: C 49.00; H 3.88.

Dimethyl 3-(3-nitrophenyl)-6,6-dimethyl-5,7-dioxa-4,8-dioxospiro[2.5]octane-2,2-dicarboxylate (VIIIb). Yield 44%, mp 110–112°C. IR spectrum (mineral oil), ν, cm^{-1}: 1720, 1745. ^1H NMR spectrum,

δ, ppm: 1.85 s (3H, CH_3), 2.06 s (3H, CH_3), 3.80 s (3H, $COOCH_3$), 3.87 s (3H, $COOCH_3$), 4.37 s (1H, CH), 7.25–8.31 m (4H, 4-BrC_6H_4). Found, %: C 52.87; H 4.00; N 2.73. $C_{187}H_{17}O_{10}$. Calculated, %: C 53.08; H 4.21; N 3.44.

Dialkyl 2-{4-[3,3-bis(alkoxycarbonyl)-1',3'-dioxospiro[cyclopropane-2,2'-indan]-1-yl]phenyl}-1',3'-dioxospiro[cyclopropane-2,2'-indan]-1,1-dicarboxylates (XIa, XIb). A mixture of 0.5 g of zinc turnings and 20 ml of THF was treated with 0.0064 mol of dibromomalonic ester, and the resulting mixture was heated until the beginning of the process. After that the reaction proceeded spontaneously. After the completion of the process the mixture obtained was refluxed for 15 min, cooled, and the organic phase was decanted into another flask, 0.0025 mol of 2-[4-(1,3-dioxoindan-2-ylidenemethyl)phenyl]methyleneindan-1,3-dione was added, and the resulting mixture was refluxed for 40–50 min. The reaction mixture was cooled, hydrolyzed with 5% acetic acid, and the reaction product was extracted with benzene. The extract was dried over Na_2SO_4, solvents were distilled off, and the residue was crystallized from methanol.

Dimethyl 2-{4-[3,3-bis(methoxycarbonyl)-1',3'-dioxospiro[cyclopropane-2,2'-indan]-1-yl]phenyl}-1',3'-dioxospiro[cyclopropane-2,2'-indan]-1,1-dicarboxylate (XIa). Yield 43%, mp 241–243°C. IR spectrum (mineral oil), ν, cm^{-1}: 1700–1745. ^1H NMR spectrum, δ, ppm: 3.60 s (6H, $2COOCH_3$), 3.69 s (6H, $2COOCH_3$), 3.89 s (2H, 2CH), 7.10–7.27 m (4H, C_6H_4), 7.80–7.90 m (8H, $2C_6H_4$). Found, %: C 65.84; H 3.72. $C_{36}H_{26}O_{12}$. Calculated, %: C 66.46; H 4.03.

Diethyl 2-{4-[3,3-bis(ethoxycarbonyl)-1',3'-dioxospiro[cyclopropane-2,2'-indan]-1-yl]phenyl}-1',3'-dioxospiro[cyclopropane-2,2'-indan]-1,1-dicarboxylate (XIb). Yield 45%, mp 109–111°C. IR spectrum (mineral oil), ν, cm^{-1}: 1700–1745. ^1H NMR spectrum, δ, ppm: 1.14 t, 1.21 t (6H, CH_3-ethyl, *J* 7.4 Hz), 1.18 t, 1.28 t (6H, CH_3-ethyl, *J* 7.4 Hz), 3.99 s (2H, 2CH), 4.16–4.22 m (8H, $4COOCH_2$, *J* 7.4 Hz), 7.19–7.23 m (4H, C_6H_4), 7.88–7.95 m (8H, $2C_6H_4$). Found, %: C 67.03; H 3.95. $C_{40}H_{34}O_{12}$. Calculated, %: C 67.98; H 4.85.

Dialkyl 2-{4-[2,2-bis(alkoxycarbonyl)-6,6-dimethyl-4,8-dioxo-5,7-dioxaspiro[2.5]oct-1-yl]phenyl}-6,6-dimethyl-4,8-dioxo-5,7-dioxaspiro[2.5]octane-1,1-dicarboxylates (XIIa, XIIb). These compounds were prepared analogously to compounds **XIa, XIb**.

Dimethyl 2-{4-[2,2-bis(methoxycarbonyl)-6,6-dimethyl-4,8-dioxo-5,7-dioxaspiro[2,5]oct-1-yl]phenyl}-6,6-dimethyl-4,8-dioxo-5,7-dioxaspiro[2.5]octane-1,1-dicarboxylate (XIIa). Yield 47%, mp 255–257°C. IR spectrum (mineral oil), ν, cm^{-1}: 1720, 1735. ^1H NMR spectrum, δ, ppm: 1.75 s (6H, $2CH_3$), 1.92 s (6H, $2CH_3$), 3.67 s (6H, $2COOCH_3$), 3.70 s (6H, $2COOCH_3$), 4.04 s (2H, 2CH), 7.262 s (4H, C_6H_4). Found, %: C 54.80; H 3.94. $C_{30}H_{30}O_{16}$. Calculated, %: C 55.73; H 4.68.

Diethyl 2-{4-[2,2-bis(ethoxycarbonyl)-6,6-dimethyl-4,8-dioxo-5,7-dioxaspiro[2,5]oct-1-yl]phenyl}-6,6-dimethyl-4,8-dioxo-5,7-dioxaspiro[2.5]octane-1,1-dicarboxylate (XIIb). Yield 53%, mp 210–212°C. IR spectrum (mineral oil), ν, cm^{-1}: 1720, 1740. ^1H NMR spectrum, δ, ppm: 1.17 q (12H, CH_3-ethyl, *J* 9.3 Hz), 1.76 s (6H, $2CH_3$), 1.94 s (6H, $2CH_3$), 4.025 s (2H, 2CH), 4.09–4.266 m (8H, CH_2OOC), 7.28 s (4H, C_6H_4). Found, %: C 57.37; H 4.84. $C_{34}H_{38}O_{16}$. Calculated, %: C 58.12; H 5.45.

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