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Reaction of 1-Aryl-2,2-dibromoalkan-1-ones with Zinc and 4-Aroyl-*1H*-Benzo[*c*]oxepin-3-ones

A. A. Glukhov[a], N. F. Kirillov[a], A. A. Potapova[a], M. I. Vakhrin[a], and O. A. Maiorova[b]

[a] *Perm State University,ul. Bukireva 15, Perm, 614990 Russia*
e-mail: kirillov@psu.ru

[b] *Institute of Technical Chemistry, Ural Branch, Russian Academy of Sciences, Perm, Russia*

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Abstract—Zinc enolates formed from the substituted 1-aryl-2,2-dibromoalkan-1-ones and zinc react with 4-aroyl-1*H*-benzo[*c*]oxepin-3-ones to form 1-alkyl-1-aroyl-1a-aroyl-1,1a,4,8b-tetrahydro-3-oxabenzo[*a*]cyclopropa[*c*]cyclohepten-2-ones.

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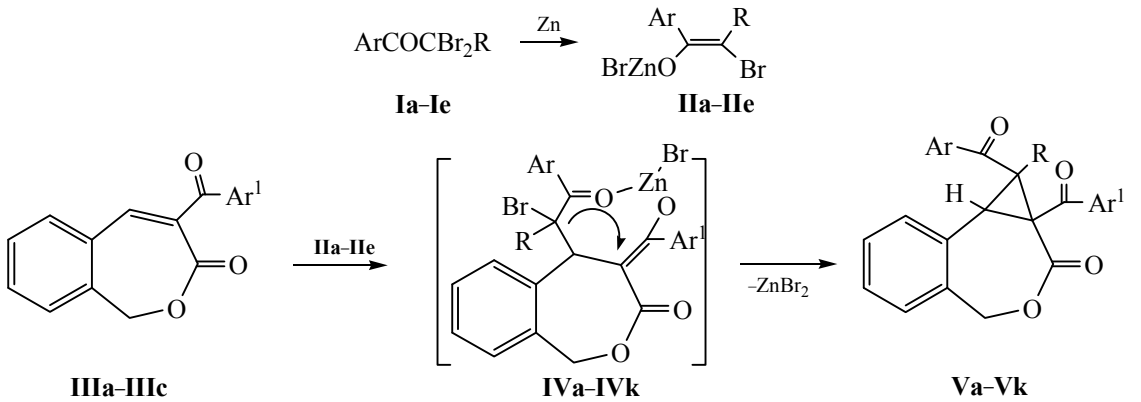
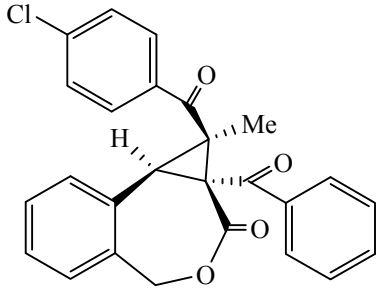
Continuing the previous study of cyclopropanation reaction with the Reformatorskii's reagents, 3-aroylchromen-2-ones, containing the activated double bond [1-3], we examined the reactions of 1-aryl-2,2-dibromoalkan-1-ones **Ia–Ie** with zinc and 4-aroyl-1*H*-benzo[*c*]oxepin-3-ones **IIIa–IIIc**. As our investigations showed, zinc-enolates **IIa–IIe**, obtained from compounds **Ia**–**Ie** and zinc, added to the double bond of compounds **IIIa**–**IIIc** to give intermediates **IVa**–**IVk**. The latter suffered the ring closure in the course of the reaction with the zinc bromide elimination to form 1-alkyl-1-aroyl-1a-aroyl-1,1a,4,8b-tetrahydro-3-oxabenzo[*a*]cyclopropa[*c*]cyclohepten-2-ones **Va–Vk**. Compounds **Va-Vk** were isolated as a single isomer in yields of 45–67%. The composition and structure of these compounds was confirmed by the elemental analysis data, IR and ^{1}H NMR spectroscopy. The IR spectra contain the characteristic absorption bands of carbonyl groups of ketone in the range of 1655–1700 cm^{-1} and lactone carbonyl groups at 1725–1735 cm^{-1}. In the ^{1}H NMR spectra there are characteristic singlets of methine protons of cyclopropane rings at 3.87–4.02 ppm and doublets of the non-equivalent methylene protons at 4.69–4.91 and 5.73–5.85 ppm.



I, II: R = Me; Ar = Ph (**a**), 4-ClC_6H_4 (**b**), 4-BrC_6H_4 (**c**). R = Et; Ar = 4-BrC_6H_4 (**d**). R = Pr; Ar = 4-BrC_6H_4 (**e**). **III**: Ar^1 = Ph (**a**), 4-BrC_6H_4 (**b**), 3-BrC_6H_4 (**c**). **IV, V**: R = Me; Ar^1 = Ph; Ar = Ph (**a**), 4-ClC_6H_4 (**b**), 4-BrC_6H_4 (**c**); Ar^1 = 4-BrC_6H_4; Ar = Ph (**d**), 4-ClC_6H_4 (**e**), 4-BrC_6H_4 (**f**). Ar^1 = 3-BrC_6H_4; Ar = 4-ClC_6H_4 (**g**), 4-BrC_6H_4 (**h**). R = Et; Ar^1 = Ph; Ar = 4-BrC_6H_4 (**i**); Ar^1 = 3-BrC_6H_4; Ar = 4-BrC_6H_4 (**j**). R = Pr; Ar^1 = Ph; Ar = 4-BrC_6H_4 (**k**).

Aiming to determine the configuration of the compounds obtained, we studied compound **Vb** as an example using the ^1H and ^{13}C NMR spectroscopy methods involving such 2D experiments as ^1H–^{13}C gHSQC, ^1H–^{13}C gHMBC and ^1H–^1H ROESY. The signals assignment in the ^1H and ^{13}C NMR spectra was made on the basis of homo- and heteronuclear 2D experiments. The carbon atom signals attribution was made after accomplishing the DEPT and gHSQC experiments. The gHMBC experiment indicates that the methine proton on C^{8b} is coupled with the carbon atoms of methyl and carbonyl groups bound to C^{1a}; and the coupling with the carbon atom of carbonyl group at C^1 is absent. The methyl group protons are strongly coupled with the carbonyl carbon atom at C^{1a} and are not coupled with the carbon C^2. In the ROESY experiment the methyl protons coupling was found with the *ortho*-protons of phenyl ring of benzoyl substituent. These data allow to conclude that the methine proton, methyl and benzoyl groups are located on the same side of the cyclopropane ring.



Vb

The similar spectral characteristics of compound **Vb** and others **Va**, **Vc–Vk** allow to assign the similar configuration to the latter.

EXPERIMENTAL

The IR spectra of compounds **Va–Vk** were obtained on a Specord-75IR spectrophotometer in mineral oil. The ^1H NMR spectra were recorded on a Mercury Plus-300 spectrometer (300 MHz) relative to internal TMS.

1-Alkyl-1-aroyl-1a-aroyl-1,1a,4,8b-tetrahydro-3-oxabenzo[*a*]cyclopropa[*c*]cyclohepten-2-ones (Va–Vk). A mixture of 0.2 g of the fine-powdered zinc, catalytic amount of mercury(II) chloride, 2 mmol of compound **IIIa–IIIc**, 2.6 mmol of **Ia–Ie**, 7.5 ml of anhydrous benzene and 2.5 ml of anhydrous ethyl acetate was refluxed for 2 h, cooled, filtered, and hydrolyzed with 5% hydrochloric acid solution. Then the organic layer was separated and the reaction products were extracted twice from the water layer with ethyl acetate. After drying the extract with anhydrous sodium sulfate the solvents were evaporated and compounds **Va–Vk** were recrystalled from the mixture ethyl acetate–hexane (2:1).

1,1a-Dibenzoyl-1-methyl-1,1a,4,8b-tetrahydro-3-oxabenzo[*a*]cyclopropa[*c*]cyclohepten-2-one (Va). Yield 0.48 g (60%), mp 172–173°C. IR spectrum, ν, cm^{-1}: 1665, 1685, 1735 (C=O). ^1H NMR spectrum, δ, ppm: 1.22 s (3H, Me), 3.87 s (1H, CH), 4.80 d, 5.73 d (2H, CH_2O, *J* 12.6 Hz), 7.15–7.60 m, 8.13 d (14H, Ar, Ph, Ph, *J* 8.0 Hz). Found, %: C 78.53; H 5.25. $C_{26}H_{20}O_4$. Calculated, %: C 78.77; H 5.09.

1a-Benzoyl-1-methyl-1-(4-chlorobenzoyl)-1,1a,4,8b-tetrahydro-3-oxabenzo[*a*]cyclopropa[*c*]cyclohepten-2-one (Vb). Yield 0.58 g (67%), mp 201–202°C. IR spectrum, ν, cm^{-1}: 1665, 1690, 1735 (C=O). ^1H NMR spectrum, δ, ppm: 1.18 s (3H, Me), 3.86 s (1H, CH), 4.88 d, 5.77 d (2H, CH_2O, *J* 12.6 Hz), 7.24–7.56 m, 8.19 d (13H, Ar, Ph, 4-ClC_6H_4, *J* 8.7 Hz). ^{13}C NMR spectrum, δ, ppm: 18.17 (Me), 37.83 (C^{8b}), 43.95 (C^1), 49.90 (C^{1a}), 69.63 (C^4), 127.86, 128.16, 128.64, 129.12, 129.56, 130.48, 130.64, 132.99, 133.19, 133.22, 134.55, 137.67, 139.68 (18C, Ar), 168.63 (C^2), 194.32 (O=*C*C^1), 195.04 (O=*C*C^{1a}). Found, %: C 72.66; H 4.53; Cl 8.06. $C_{26}H_{19}ClO_4$. Calculated, %: C 72.47; H 4.44; Cl 8.23.

1a-Benzoyl-1-(4-bromobenzoyl)-1-methyl-1,1a,4,8b-tetrahydro-3-oxabenzo[*a*]cyclopropa[*c*]cyclohepten-2-one (Vc). Yield 0.54 g (57%), mp 201–202°C. IR spectrum, ν, cm^{-1}: 1660, 1690, 1735 (C=O). ^1H NMR spectrum, δ, ppm: 1.20 s (3H, Me), 3.88 s (1H, CH), 4.89 d, 5.78 d (2H, CH_2O, *J* 12.6 Hz), 7.31–7.60 m, 8.13 d (13H, Ar, Ph, 4-BrC_6H_4, *J* 8.4 Hz). Found, %: C 65.82; H 4.18; Br 17.02. $C_{26}H_{19}BrO_4$. Calculated, %: C 65.70; H 4.03; Br 16.81.

1-Benzoyl-1a-(4-bromobenzoyl)-1-methyl-1,1a,4,8b-tetrahydro-3-oxabenzo[*a*]cyclopropa[*c*]cyclohepten-2-one (Vd). Yield 0.54 g (57%), mp 182–183°C. IR spectrum, ν, cm^{-1}: 1655, 1680, 1730 (C=O). ^1H NMR spectrum, δ, ppm: 1.28 s (3H, Me), 3.92 s (1H, CH), 4.86 d, 5.78 d (2H, CH_2O, *J* 12.6 Hz), 7.32–7.60 m, 8.18 d (13H, Ar, Ph, 4-BrC_6H_4, *J* 8.4 Hz). Found, %: C 65.54; H 3.94; Br 16.97. $C_{26}H_{19}BrO_4$. Calculated, %: C 65.70; H 4.03; Br 16.81.

1a-(4-Bromobenzoyl)-1-methyl-1-chlorobenzoyl-1,1a,4,8b-tetrahydro-3-oxabenzo[*a*]cyclopropa[*c*]-cyclohepten-2-one (Ve). Yield 0.59 g (58%), mp 215–

217°C. IR spectrum, ν, cm^{-1}: 1655, 1695, 1735 (C=O). ^1H NMR spectrum, δ, ppm: 1.22 s (3H, Me), 3.89 s (1H, CH), 4.89 d, 5.76 d (2H, CH_2O, *J* 12.3 Hz), 7.32–7.60 m, 8.16 d (12H, Ar, 4-ClC_6H_4, 4-BrC_6H_4, *J* 8.4 Hz). Found, %: C 61.40; H 3.67. $C_{26}H_{18}BrClO_4$. Calculated, %: C 61.26; H 3.56.

1,1a-Bis-(4-bromobenzoyl)-1-methyl-1,1a,4,8b-tetrahydro-3-oxabenzo[*a*]cyclopropa[*c*]cyclohepten-2-one (Vf). Yield 0.69 g (62%), mp 212–214°C. IR spectrum, ν, cm^{-1}: 1655, 1690, 1730 (C=O). ^1H NMR spectrum, δ, ppm: 1.22 s (3H, Me), 3.89 s (1H, CH), 4.88 d, 5.76 d (2H, CH_2O, *J* 12.6 Hz), 7.34 d, 7.44–7.52 m, 7.56 d, 7.59 d, 8.08 d (12H, Ar, 4-BrC_6H_4, 4-BrC_6H_4, *J* 8.7 Hz). Found, %: C 56.60; H 3.39; Br 28.58. $C_{26}H_{18}Br_2O_4$. Calculated, %: C 56.34; H 3.27; Br 28.83.

1a-(3-Bromobenzoyl)-1-methyl-1-chlorobenzoyl-1,1a,4,8b-tetrahydro-3-oxabenzo[*a*]cyclopropa[*c*]-cyclohepten-2-one (Vg). Yield 0.46 g (45%), mp 182–183°C. IR spectrum, ν, cm^{-1}: 1680, 1700, 1725 (C=O). ^1H NMR spectrum, δ, ppm: 1.22 s (3H, Me), 3.97 s (1H, CH), 4.69 d, 5.85 d (2H, CH_2O, *J* 12.6 Hz), 7.26–7.40 m, 7.48 t, 7.52 d, 7.58 t, 8.35 d (12H, Ar, 4-ClC_6H_4, 3-BrC_6H_4, *J* 8.4 Hz). Found, %: C 61.09; H 3.44. $C_{26}H_{18}BrClO_4$. Calculated, %: C 61.26; H 3.56.

1a-(3-Bromobenzoyl)-1-(4-bromobenzoyl)-1-methyl-1,1a,4,8b-tetrahydro-3-oxabenzo[*a*]cyclopropa-[*c*]cyclohepten-2-one (Vh). Yield 0.52 g (47%), mp 183–184°C. IR spectrum, ν, cm^{-1}: 1680, 1695, 1730 (C=O). ^1H NMR spectrum, δ, ppm: 1.21 s (3H, Me), 3.96 s (1H, CH), 4.69 d, 5.84 d (2H, CH_2O, *J* 12.6 Hz), 7.26–7.36 m, 7.38 d, 7.47 t, 7.58 t, 7.69 d, 8.27 d (12H, Ar, 3-BrC_6H_4, 4-BrC_6H_4, *J* 8.4 Hz). Found, %: C 56.53; H 3.42; Br 28.59. $C_{26}H_{18}Br_2O_4$. Calculated, %: C 56.34; H 3.27; Br 28.83.

1a-Benzoyl-1-(4-bromobenzoyl)-1-ethyl-1,1a,4,8b-tetrahydro-3-oxabenzo[*a*]cyclopropa[*c*]cyclohepten-2-one (Vi). Yield 0.58 g (59%), mp 192–193°C. IR spectrum, ν, cm^{-1}: 1675, 1695, 1730 (C=O). ^1H NMR spectrum, δ, ppm: 0.77 t (3H, C$H_3$$CH_2$, *J* 7.2 Hz), 0.91 q.t, 2.09 q.d (2H, CH_3CH_2, *J* 7.2 Hz, *J* 21 Hz), 3.95 s (1H, CH), 4.91 d, 5.75 d (2H, CH_2O, *J* 12.6 Hz), 7.32–7.51 m, 7.54 d, 7.59 d, 7.68 d, 8.17 d (13H, Ar, Ph, 4-BrC_6H_4, *J* 8.4 Hz). Found, %: C 65.99; H 4.44; Br 16.12. $C_{27}H_{21}BrO_4$. Calculated, %: C 66.27; H 4.33; Br 16.33.

1a-(3-Bromobenzoyl)-1-(4-bromobenzoyl)-1-ethyl-1,1a,4,8b-tetrahydro-3-oxabenzo[*a*]cyclopropa[*c*]-cyclohepten-2-one (Vj). Yield 0.52 g (46%), mp 202–204°C. IR spectrum, ν, cm^{-1}: 1680, 1700, 1725 (C=O). ^1H NMR spectrum, δ, ppm: 0.76 t (3H, C$H_3$$CH_2$, *J* 7.2 Hz), 0.91 q. d, 2.15 q. d (2H, CH_3CH_2, *J* 7.2 Hz, *J* 21 Hz), 4.02 s (1H, CH), 4.69 d, 5.80 d (2H, CH_2O, *J* 12.9 Hz), 7.24–7.34 m, 7.36 d, 7.47 t, 7.58 t, 7.66 d, 7.69 d, 8.30 d (12H, Ar, 3-BrC_6H_4, 4-BrC_6H_4, *J* 8.4 Hz). Found, %: C 56.89; H 3.63; Br 28.35. $C_{27}H_{20}Br_2O_4$. Calculated, %: C 57.07; H 3.55; Br 28.12.

1a-Benzoyl-1-(4-bromobenzoyl)-1-propyl-1,1a,4,8b-tetrahydro-3-oxabenzo[*a*]cyclopropa[*c*]cyclohepten-2-one (Vk). Yield 0.53 g (53%), mp 211–213°C. IR spectrum, ν, cm^{-1}: 1675, 1685, 1730 (C=O). ^1H NMR spectrum, δ, ppm: 0.54 t (3H, C$H_3$$CH_2$$CH_2$, *J* 7.2 Hz), 0.91 t. d, 2.09 t. d (2H, CH_3CH_2CH_2 , *J* 4.2 Hz, *J* 13.2 Hz), 1.01–1.42 m (2H, CH_3C$H_2$$CH_2$), 3.94 s (1H, CH), 4.90 d, 5.74 d (2H, CH_2O, *J* 12.6 Hz), 7.31–7.51 m, 7.53 d, 7.59 d, 7.66 d, 8.17 d (13H, Ar, Ph, 4-BrC_6H_4, *J* 8.4 Hz). Found, %: C 67.05; H 4.73; Br 16.09. $C_{28}H_{23}BrO_4$. Calculated, %: C 66.81; H 4.61; Br 15.87.

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