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Cyclopropanation of 3-(2-Oxo-2*H*-chromen-3-ylcarbonyl)-2*H*-chromen-2-one with Zinc Enolates Derived from 1-Aryl-2,2-dibromoalkanones

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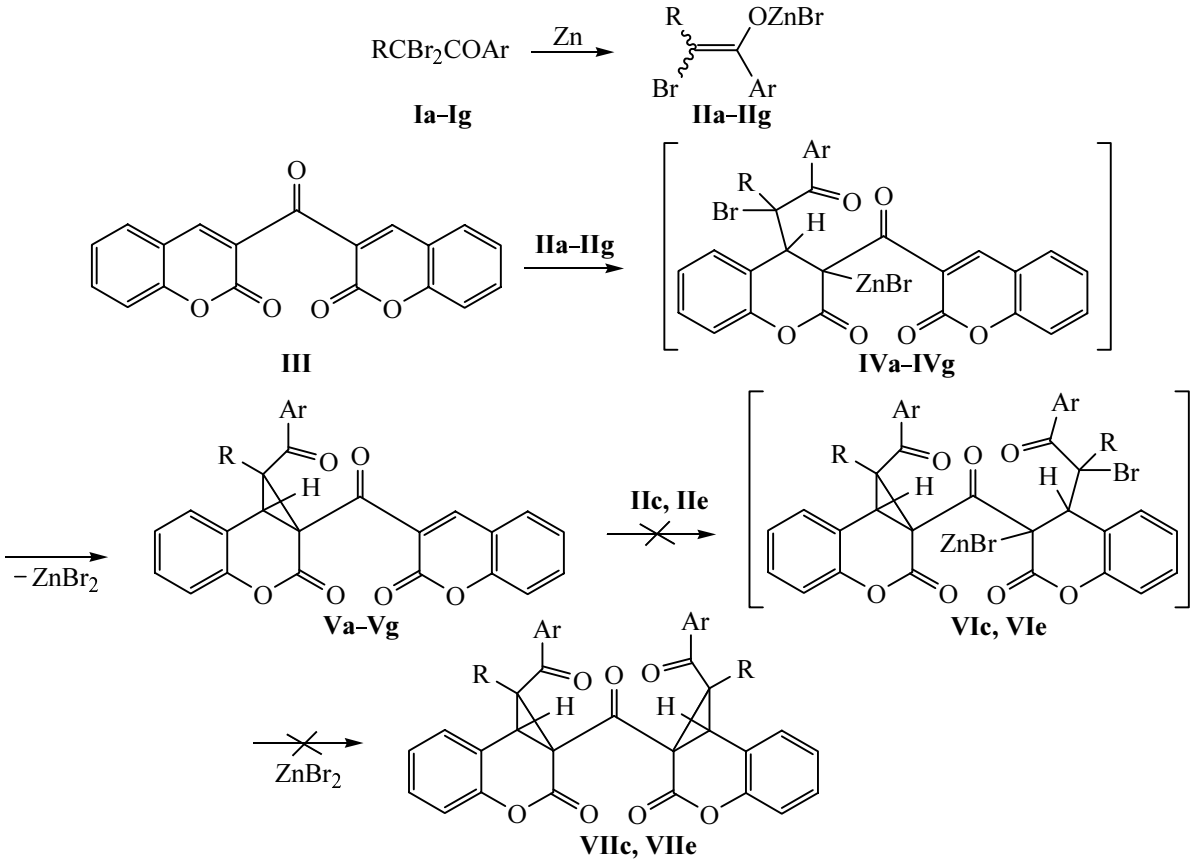
Abstract—Zinc enolates derived from 1-aryl-2,2-dibromoalkanones react with 3-(2-oxo-2*H*-chromen-3-ylcarbonyl)-2*H*-chromen-2-one to give 1-alkyl-1-aroyl-1a-(2-oxo-2*H*-chromen-3-ylcarbonyl)-1a,7b-dihydrocyclopropa[*c*]-chromen-2(1*H*)-ones as a single stereoisomer.

We previously found that bromine-containing zinc enolates react with 3-acetyl-6-bromochromen-2-one to give 1a-acetyl-1-alkyl-1-aroyl-6-bromo-1a,7b-dihydrocyclopropa[*c*]chromen-2(1*H*)-ones [1]. In order to further extend the scope of application of this method for cyclopropanation of substrates possessing an activated double bond, in the present work we examined reactions of 3-(2-oxo-2*H*-chromen-3-ylcarbonyl)-2*H*-chromen-2-one with zinc enolates **IIa**–**IIg** derived from dibromo ketones **Ia**–**Ig** (Scheme 1).

Scheme 1.



R = Me, Ar = 4-MeC_6H_4 (**a**), 4-FC_6H_4 (**b**), 4-ClC_6H_4 (**c**), 4-BrC_6H_4 (**d**); R = Et, Ar = Ph (**e**), 4-FC_6H_4 (**f**), 4-ClC_6H_4 (**g**).

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In the first stage, zinc enolates **IIa**–**IIg** add at one double bond in compound **III** to give intermediates **IVa**–**IVg** which undergo spontaneous cyclization with formation of fused cyclopropane derivatives, 1-alkyl-1-aroyl-1a-(2-oxo-2*H*-chromen-3-ylcarbonyl)-1a,7b-dihydrocyclopropa[*c*]chromen-2(1*H*)-ones **Va**–**Vg**, in 64–74% yield. We also expected that increase in the zinc enolate-to-substrate ratio (e.g., from 1:1.5 to 1:3) would lead to formation of bis-cyclopropanation products **VII** through intermediates **VI**. However, in the reactions of **III** with excess zinc enolates **IIc** and **IIe** we isolated only monocyclopropane derivatives **Vc** and **Ve**. Presumably, the reason is considerable steric hindrances created by the cyclopropane fragment in **V** to addition of zinc enolate at the activated double bond in the second chromene fragment.

The structure of compounds **Va**–**Vg** was confirmed by the data of elemental analysis and IR and ^{1}H NMR spectroscopy. The IR spectra of **Va**–**Vg** contain characteristic carbonyl absorption bands at 1670–1680 (COAr, COC=C) and 1725–1740 cm^{-1} (COO). In the ^{1}H NMR spectra of these compounds, apart from other signals, we observed singlets at δ 3.69–3.73 and 8.10–8.18 ppm, which belong to the 7b-H and 4'-H protons, respectively. The presence of only one set of signals for each compound **V** indicates formation of a single stereoisomer (with respect to the cyclopropane ring plane).

EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrometer from samples dispersed in mineral oil. The ^{1}H NMR spectra were recorded on a Tesla BS-576A spectrometer (80 MHz) from solutions in $CDCl_3$; the chemical shifts were measured relative to hexamethyldisiloxane as internal reference.

1-Alkyl-1-aroyl-1a-(2-oxo-2*H*-chromen-3-ylcarbonyl)-1a,7b-dihydrocyclopropa[*c*]chromen-2(1*H*)-ones Va–Vg (*general procedure***).** A solution of 0.0075 mol of dibromo ketone **Ia**–**Ig** in 3 ml of ethyl acetate was added to a mixture of 2 g of zinc (prepared as fine turnings), 8 ml of diethyl ether, and 5 ml of ethyl acetate. The mixture was heated to initiate the reaction, and it then occurred spontaneously. When the reaction was complete, the mixture was heated for 15 min on a water bath and cooled, and the liquid phase was separated from unreacted zinc by decanting into another flask. Compound **III**, 0.005 mol, and 25 ml of ethyl acetate were added, and the mixture was heated for 30 min on a water bath, cooled, treated with 5% hydrochloric acid, and extracted with diethyl ether. The extract was dried over sodium sulfate and evaporated, and the residue was recrystallized thrice from a mixture of ethyl acetate, carbon tetrachloride, and methanol at a ratio of 1:1:3. In the synthesis of compounds **Vc** and **Ve,** 0.015 mol of dibromo ketone **IIc** or **IIe** was used.

1-Methyl-1-(4-methylbenzoyl)-1a-(2-oxo-2*H*-chromen-3-ylcarbonyl)-1a,7b-dihydrocyclopropa[*c*]chromen-2(1*H*)-one (Va). Yield 74%, mp 149–150°C. ^{1}H NMR spectrum, δ, ppm: 1.22 s (3H, Me), 2.33 s (3H, 4-**Me**C_6H_4), 3.73 s (1H, CH), 6.90–7.80 m (12H, C_6H_4, MeC_6**H**$_4$), 8.18 s (1H, CH=). Found, %: C 74.85; H 4.26. $C_{29}H_{20}O_6$. Calculated, %: C 74.99; H 4.34.

1-(4-Fluorobenzoyl)-1-methyl-1a-(2-oxo-2*H*-chromen-3-ylcarbonyl)-1a,7b-dihydrocyclopropa[*c*]chromen-2(1*H*)-one (Vb). Yield 65%, mp 155–157°C. ^{1}H NMR spectrum, δ, ppm: 1.21 s (3H, Me), 3.71 s (1H, CH), 6.90–7.90 m (12H, C_6H_4, 4-FC_6H_4), 8.15 s (1H, CH=). Found, %: C 71.92; H 3.58. $C_{28}H_{17}FO_6$. Calculated, %: C 71.79; H 3.66.

1-(4-Chlorobenzoyl)-1-methyl-1a-(2-oxo-2*H*-chromen-3-ylcarbonyl)-1a,7b-dihydrocyclo-propa[*c*]chromen-2(1*H*)-one (Vc). Yield 67%, mp 160–162°C. ^{1}H NMR spectrum, δ, ppm: 1.21 s (3H, Me), 3.70 s (1H, CH), 6.90–7.90 m (12H, C_6H_4, 4-ClC_6H_4), 8.16 s (1H, CH=). Found, %: C 69.22; H 3.46. $C_{28}H_{17}ClO_6$. Calculated, %: C 69.36; H 3.53.

1-(4-Bromobenzoyl)-1-methyl-1a-(2-oxo-2*H*-chromen-3-ylcarbonyl)-1a,7b-dihydrocyclo-propa[*c*]chromen-2(1*H*)-one (Vd). Yield 71%, mp 162–163°C. ^{1}H NMR spectrum, δ, ppm: 1.21 s (3H, Me), 3.71 s (1H, CH), 6.90–7.80 m (12H, C_6H_4, 4-BrC_6H_4), 8.17 s (1H, CH=). Found, %: C 63.41; H 3.30. $C_{28}H_{17}BrO_6$. Calculated, %: C 63.53; H 3.24.

1-Benzoyl-1-ethyl-1a-(2-oxo-2*H*-chromen-3-ylcarbonyl)-1a,7b-dihydrocyclopropa[*c*]chromen-2(1*H*)-one (Ve). Yield 64%, mp 134–136°C. ^{1}H NMR spectrum, δ, ppm: 0.43 t (3H, CH_2C**H**$_3$, J = 7 Hz), 1.30 m, 2.10 m (2H, C**H**$_2$CH$_3$), 3.71 s (1H, CH), 6.90–7.90 m (13H, C_6H_4, C_6H_5), 8.10 s (1H, CH=). Found, %: C 74.85; H 4.39. $C_{29}H_{20}O_6$. Calculated, %: C 74.99; H 4.34.

1-Ethyl-1-(4-fluorobenzoyl)-1a-(2-oxo-2*H*-chromen-3-ylcarbonyl)-1a,7b-dihydrocyclo-propa[*c*]chromen-2(1*H*)-one (Vf). Yield 65%, mp 126–127°C. ^{1}H NMR spectrum, δ, ppm: 0.45 t (3H, CH_2C**H**$_3$,

J = 7 Hz), 1.30 m, 2.10 m (2H, C**H**$_2$CH$_3$), 3.69 s (1H, CH), 6.90–7.95 m (12H, C_6H_4, 4-FC_6H_4), 8.10 s (1H, CH=). Found, %: C 72.01; H 3.87. $C_{29}H_{19}FO_6$. Calculated, %: C 72.20; H 3.97

1-(4-Chlorobenzoyl)-1-ethyl-1a-(2-oxo-2*H*-chromen-3-ylcarbonyl)-1a,7b-dihydrocyclopropa-[*c*]chromen-2(1*H*)-one (Vg). Yield 70%, mp 174–175°C. ^{1}H NMR spectrum, δ, ppm: 0.45 t (3H, CH$_2$C**H**$_3$, *J* = 7 Hz), 1.30 m, 2.10 m (2H, C**H**$_2$CH$_3$), 3.69 s (1H, CH), 6.90–7.90 m (12H, C_6H_4, 4-ClC_6H_4), 8.10 s (1H, CH=). Found, %: C 69.70; H 3.71. $C_{29}H_{19}ClO_6$. Calculated, %: C 69.81; H 3.84.

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