

# Reactions of Zinc Enolates Derived from 1-Aryl-2,2-dibromoalkanones with 2-Acyl-3*H*-benzo[*f*]chromen-3-ones, 6-Bromo-2-oxochromene-3-carboxamides, and 3-Oxo-3*H*-benzo[*f*]chromene-2-carboxamides

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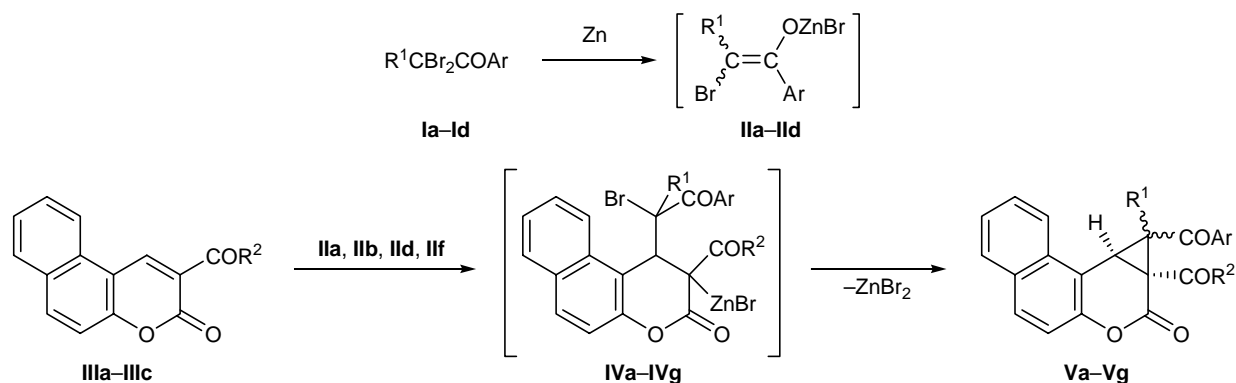
Received June 30, 2003

**Abstract**—Zinc enolates derived from substituted 1-aryl-2,2-dibromoalkanones reacted with 2-acyl-3*H*-benzo[*f*]chromen-3-ones to give 1-alkyl-1-aryl-1a-acyl-1a,9c-dihydro-1*H*-3-oxacyclopropa[*c*]phenanthren-2-ones which were formed as a single stereoisomer. Reactions of the same zinc enolates with 6-bromo-2-oxochromene-3-carboxamides (piperidides and morpholides) afforded 1-aryl-6-bromo-1-alkyl-1a-piperidino-(morpholino)carbonyl-1a,7b-dihydrocyclopropa[*c*]chromen-2-ones with high stereoselectivity. Likewise, 1-benzoyl-1-methyl-1a-morpholinocarbonyl-1a,9c-dihydro-1*H*-3-oxacyclopropa[*c*]phenanthren-2-one was obtained by reaction with 3-oxo-3*H*-benzo[*f*]chromene-2-carboxylic acid morpholide.

Reactions of 3-acyl-2*H*-1-benzopyran-2-ones with phenacyl bromide in the presence of bases were reported to give cyclopropane derivatives [1]. In continuation of our studies on cyclopropanation of heterocyclic compounds [2], in the present work we examined reactions of 2-acyl-3*H*-benzo[*f*]chromen-3-ones **IIIa–IIIc** with bromine-containing zinc enolates **Ia, Ib, Id**, and **If**, which were prepared from

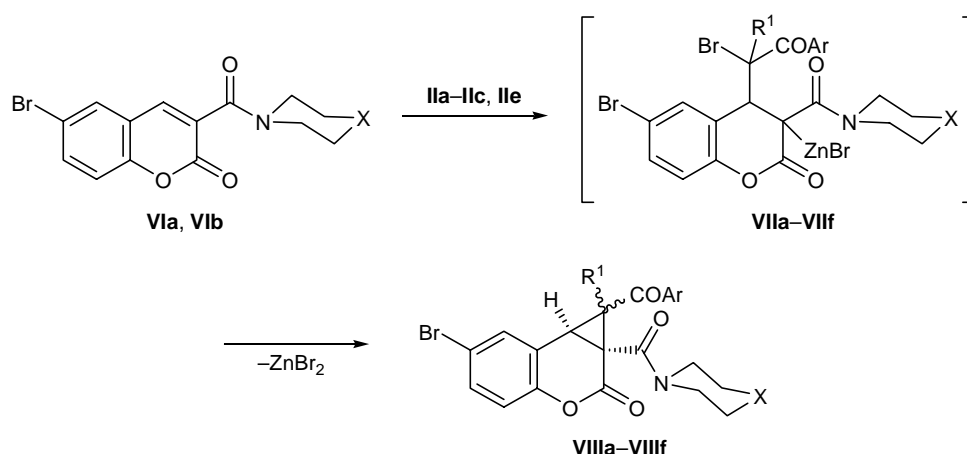
1-aryl-2,2-dibromoalkanones **Ia, Ib, Id**, and **If** and zinc. The results showed that nucleophilic zinc enolates are capable of adding at the C<sup>4</sup> atom of the heteroring in spite of steric hindrances created by the fused benzene ring. Intermediates **IVa–IVg** thus formed undergo spontaneous intramolecular cyclization to 1-alkyl-1-aryl-1a-acyl-1a,9c-dihydro-1*H*-3-oxacyclopropa[*c*]phenanthren-2-ones **Va–Vg** (Scheme 1,

Scheme 1.



**I, II**, R<sup>1</sup> = Me, Ar = Ph (**a**), 4-MeC<sub>6</sub>H<sub>4</sub> (**b**), 4-EtC<sub>6</sub>H<sub>4</sub> (**c**), 4-BrC<sub>6</sub>H<sub>4</sub> (**d**); R<sup>1</sup> = Et, Ar = Ph (**e**), 4-ClC<sub>6</sub>H<sub>4</sub> (**f**); **III**, R<sup>2</sup> = Me (**a**), Ph (**b**), 2-furyl (**c**); **IV, V**, R<sup>1</sup> = R<sup>2</sup> = Me, Ar = 4-MeC<sub>6</sub>H<sub>4</sub> (**a**), 4-BrC<sub>6</sub>H<sub>4</sub> (**b**); R<sup>1</sup> = Me, R<sup>2</sup> = Ar = Ph (**c**); Ar = 4-MeC<sub>6</sub>H<sub>4</sub> (**d**); R<sup>1</sup> = Et, R<sup>2</sup> = Ph, Ar = ClC<sub>6</sub>H<sub>4</sub> (**e**); R<sup>1</sup> = Me, R<sup>2</sup> = 2-furyl, Ar = Ph (**f**), 4-MeC<sub>6</sub>H<sub>4</sub> (**g**).

Scheme 2.



**VI**, X =  $\text{CH}_2$  (**a**), O (**b**); **VII**, **VIII**,  $\text{R}^1$  = Me, X =  $\text{CH}_2$ , Ar = Ph (**a**), 4-MeC<sub>6</sub>H<sub>4</sub> (**b**), 4-EtC<sub>6</sub>H<sub>4</sub> (**c**); X = O, Ar = Ph (**d**), 4-EtC<sub>6</sub>H<sub>4</sub> (**e**);  $\text{R}^1$  = Et, X = O, Ar = Ph (**f**).

Scheme 3.

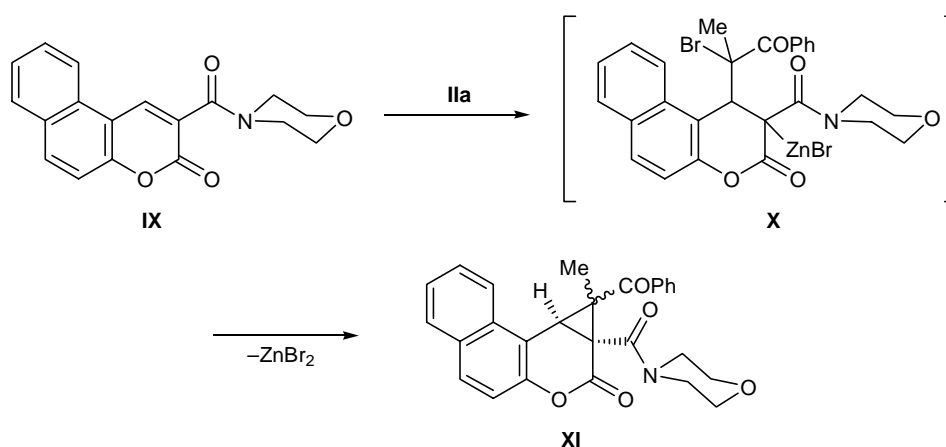
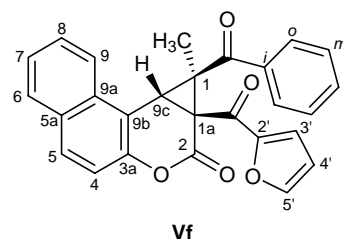


Table 1). The nature of the acyl group does not affect the yield of compounds **Va-Vd**, **Vf**, and **Vg** to an appreciable extent, and it ranges from 48 to 67%. On the other hand, the reaction is sensitive to steric effects of substituents in the nucleophile. Replacement of  $\text{R}^1$  = Me in **II** by  $\text{R}^1$  = Et leads to sharp decrease in the yield of final product **Ve** to 28%. In the other cases, we failed to isolate products in the reactions with zinc enolates derived from 1-aryl-2,2-dibromobutanones **I** where  $\text{R}^1$  = Et.

The structure of compounds **Va-Vg** was proved by elemental analysis and  $^1\text{H}$  NMR and IR spectroscopy. The IR spectra of **Vc-Vg** contained absorption bands at 1680 and 1725–1750  $\text{cm}^{-1}$ , which are typical of carbonyl stretching vibrations of the aroyl, furoyl, and lactone moieties. Compounds **Va** and **Vb** also showed in the IR spectra absorption bands at 1685–1710  $\text{cm}^{-1}$ ,

which belong to stretching vibrations of the acetyl carbonyl group. In the  $^1\text{H}$  NMR spectra of **Va-Vg** we observed only one singlet from the 9c-H proton at  $\delta$  4.07–4.43 ppm. This indicates that compounds **Va-Vg** were isolated as a single stereoisomer (Table 2).

The structure and configuration of the obtained cyclopropane derivatives were established on the basis of one- and two-dimensional  $^1\text{H}$  and  $^{13}\text{C}$  spectra using compound **Vf** as an example. The assignment of



**Table 1.** Yields, constants, and elemental analyses of 1a-acyl-1-alkyl-1-aro-yl-1a,9c-dihydro-1*H*-3-oxacyclopropa[*c*]phenanthren-2-ones **Va–Vg**, 1-alkyl-1-aro-yl-6-bromo-1a-piperidinocarbonyl-1a,7b-dihydrocyclopropa[*c*]chromen-2-ones **VIIIa–VIIIc**, and 1-alkyl-1-aro-yl-6-bromo-1a-morpholinocarbonyl-1a,7b-dihydrocyclopropa[*c*]chromen-2-ones **VIIIId–VIIIf**

Comp. no.	Yield, %	mp, °C	Found, %		Formula	Calculated, %	
			C	H		C	H
<b>Va</b>	59	196–197	78.03	5.20	C <sub>25</sub> H <sub>20</sub> O <sub>4</sub>	78.11	5.24
<b>Vb</b>	48	204–205	64.08	3.72	C <sub>24</sub> H <sub>17</sub> O <sub>4</sub> Br	64.16	3.81
<b>Vc</b>	67	247–248	80.61	4.69	C <sub>29</sub> H <sub>20</sub> O <sub>4</sub>	80.54	4.66
<b>Vd</b>	64	212–213	81.38	4.16	C <sub>30</sub> H <sub>18</sub> O <sub>4</sub>	81.44	4.10
<b>Ve</b>	28	230–231	74.81	4.32	C <sub>30</sub> H <sub>21</sub> O <sub>4</sub> Cl	74.92	4.40
<b>Vf</b>	51	234–235	77.47	4.11	C <sub>28</sub> H <sub>18</sub> O <sub>5</sub>	77.41	4.18
<b>Vg</b>	65	172–174	77.60	4.57	C <sub>29</sub> H <sub>20</sub> O <sub>5</sub>	77.67	4.50
<b>VIIIa</b>	55	179–182	61.42	4.65	C <sub>24</sub> H <sub>22</sub> BrNO <sub>4</sub>	61.55	4.73
<b>VIIIb</b>	43	202–206	62.11	4.95	C <sub>25</sub> H <sub>24</sub> BrNO <sub>4</sub>	62.25	5.01
<b>VIIIc</b>	51	262–264	62.89	5.19	C <sub>26</sub> H <sub>26</sub> BrNO <sub>4</sub>	62.91	5.28
<b>VIIId</b>	61	206–209	58.60	4.21	C <sub>23</sub> H <sub>20</sub> BrNO <sub>5</sub>	58.74	4.29
<b>VIIIe</b>	50	240–242	60.14	4.79	C <sub>25</sub> H <sub>24</sub> BrNO <sub>5</sub>	60.25	4.85
<b>VIIIf</b>	40	212–213	59.40	4.48	C <sub>24</sub> H <sub>22</sub> BrNO <sub>5</sub>	59.52	4.58

signals in the <sup>1</sup>H NMR spectra was confirmed by analysis of their multiplicity; it was consistent with the data of two-dimensional homonuclear COSY and ROESY experiments. Signals from carbon atoms attached to hydrogen were unambiguously identified by the corresponding cross peaks in the 2D HETCOR spectrum, and those from quaternary carbon atoms were assigned on the basis of the 2D HMBC spectra using <sup>2</sup>J<sub>HC</sub> and <sup>3</sup>J<sub>HC</sub> correlations.

Mutual arrangement of the 9c-H atom and methyl group on C<sup>1</sup> was determined by detailed analysis of the 2D-ROESY spectrum which contained cross peaks between the following protons: 9c-H and 9-H, 9c-H and 1-CH<sub>3</sub>, and 1-CH<sub>3</sub> and *o*-H. Taking into account the small size of the three-membered ring, the presence of a cross peak between 9c-H and 1-CH<sub>3</sub> cannot be regarded as a proof for *cis* or *trans* configuration of these groups. However, comparison of the relative intensities of the cross peaks (which were determined by volume integration of the 2D-ROESY spectrum showed that (9c-H/9-H) ≫ (9c-H/1-CH<sub>3</sub>); this means that the 9c-H atom and the 1-CH<sub>3</sub> group in molecule **Vf** are arranged *trans*. This conclusion was confirmed by measuring the stationary Overhauser effect in the 1D-difference NOE experiment: saturation of the 9c-H signal produces a positive NOE on 9-H (η<sub>NOE</sub> = 15%), while the intensity of the methyl proton signal does not change (η = 0).

Detailed mechanism of formation of cyclopropanes **Va–Vg** has not been established so far. Presumably, the transformation of intermediates **IVa–IVg** follows a common mechanism, according to which the cyclization leads to formation of a single stereoisomer of **V** with *trans* arrangement of 9c-H and alkyl substituent on the C<sup>1</sup> atom.

We also examined the reactivity of bromine-containing zinc enolates toward compounds having an activated double bond. For this purpose, zinc enolates **IIa–IIc** and **IIe** obtained from 1-aryl-2,2-dibromoalkanones **Ia–Ic** and **Ie**, respectively, were brought into reaction with 6-bromo-2-oxochromene-3-carboxamides **VIa** and **VIb** and 3-oxo-3*H*-benzo[*f*]chromene-2-carboxylic acid morpholide (**IX**). According to our previous data, in the first reaction stage bromine-containing zinc enolates as soft nucleophiles add at the electron-deficient C<sup>4</sup> atom of alkyl 6-bromo-2-oxochromene-3-carboxylates [2]. The amide group activates the double bond to a lesser extent than does ester group. Nevertheless, this effect is sufficient to ensure addition of zinc enolates **IIa–IIc** and **IIe** at the C<sup>4</sup> atom of heterocycles **VIa** and **VIb** to give intermediates **VIIa–VIIf**. Spontaneous intramolecular cyclization of the latter resulted in formation of 1-aro-yl-1-alkyl-6-bromo-1a-piperidinocarbonyl-1a,7b-dihydrocyclopropa[*c*]chromen-2-ones **VIIIa–VIIIc** and 1-aro-yl-1-alkyl-6-bromo-1a-morpholinocarbonyl-

**Table 2.** IR and  $^1\text{H}$  NMR spectra of 1a-acyl-1-alkyl-1-aroyle-1a,9c-dihydro-1*H*-3-oxacyclopropa[*c*]phenanthren-2-ones **Va–Vg**, 1-alkyl-1-aroyle-6-bromo-1a-piperidinocarbonyl-1a,7b-dihydrocyclopropa[*c*]chromen-2-ones **VIIIa–VIIIc**, and 1-alkyl-1-aroyle-6-bromo-1a-morpholinocarbonyl-1a,7b-dihydrocyclopropa[*c*]chromen-2-ones **VIIIId–VIIIf**

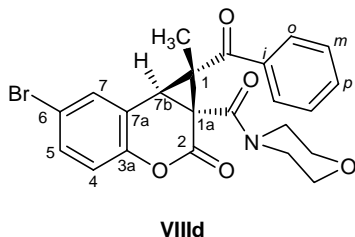
Comp. no.	IR spectrum, $\nu$ , $\text{cm}^{-1}$			$^1\text{H}$ NMR spectrum, $\delta$ , ppm ( <i>J</i> , Hz)
	COAr	COMe	C <sup>2</sup> =O	
<b>Va</b>	1680	1710	1725	1.23 s (3H, Me), 2.45 s (3H, 4-MeC <sub>6</sub> H <sub>4</sub> ), 2.46 s (3H, COMe), 4.08 s (1H, CH), 7.25–8.35 m (10H, C <sub>10</sub> H <sub>6</sub> , 4-MeC <sub>6</sub> H <sub>4</sub> )
<b>Vb</b>		1690	1730	1.21 s (3H, Me), 2.46 s (3H, COMe), 4.07 s (1H, CH), 7.25–8.35 m (10H, C <sub>10</sub> H <sub>6</sub> , 4-BrC <sub>6</sub> H <sub>4</sub> )
<b>Vc</b>		1690	1725	1.40 s (3H, Me), 4.42 s (1H, CH), 7.40–8.30 m (16H, C <sub>10</sub> H <sub>6</sub> , Ph, Ph)
<b>Vd</b>		1685	1725	1.40 s (3H, Me), 2.47 s (3H, 4-MeC <sub>6</sub> H <sub>4</sub> ), 4.37 s (1H, CH), 7.40–8.30 m (15H, C <sub>10</sub> H <sub>6</sub> , 4-MeC <sub>6</sub> H <sub>4</sub> , Ph)
<b>Ve</b>	1680		1750	0.30 t (3H, CH <sub>3</sub> CH <sub>2</sub> ), 1.15 m and 2.18 m (2H, CH <sub>3</sub> CH <sub>2</sub> ), 4.31 s (1H, CH), 7.40–8.30 m (15H, C <sub>10</sub> H <sub>6</sub> , 4-ClC <sub>6</sub> H <sub>4</sub> , Ph)
<b>Vf</b>	1680		1740	1.12 s (3H, Me), 4.42 s (1H, 9c-H), 6.72 d.d (1H, 4'-H, <i>J</i> = 3.7, 1.7), 7.32 d (1H, 3'-H, <i>J</i> = 3.7), 7.53 d (1H, 4-H, <i>J</i> = 8.9), 7.62 m (3H, <i>m</i> -H, 7-H), 7.68 m (1H, <i>p</i> -H), 7.93 m (2H, <i>o</i> -H), 8.00 d (1H, 5'-H, <i>J</i> = 1.7), 8.07 d (1H, 6-H, <i>J</i> = 8.1), 8.10 d (1H, 5-H, <i>J</i> = 8.9), 8.20 d (1H, 9-H, <i>J</i> = 8.4)
<b>Vg</b>	1680		1740	1.13 s (3H, Me), 2.45 s (3H, 4-MeC <sub>6</sub> H <sub>4</sub> ), 4.43 s (1H, CH), 6.70–8.20 m (8H, C <sub>4</sub> H <sub>4</sub> O, 4-MeC <sub>6</sub> H <sub>4</sub> )
<b>VIIIa</b>	1640	1660	1750	1.13 s (3H, Me); 1.50 m, 1.62 m, and 3.15–3.50 m (10H, C <sub>5</sub> H <sub>10</sub> N); 3.91 s (1H, CH); 7.12 d, 7.45–7.56 m, and 7.75–7.82 m (8H, C <sub>6</sub> H <sub>3</sub> , Ph)
<b>VIIIb</b>	1640	1660	1750	1.13 s (3H, Me); 1.50 m, 1.62 m, and 3.15–3.50 m (10H, C <sub>5</sub> H <sub>10</sub> N); 2.45 s (3H, 4-MeC <sub>6</sub> H <sub>4</sub> ); 3.86 s (1H, CH); 7.12 d, 7.30 d, 7.53 d, 7.70 d, and 7.76 s (7H, C <sub>6</sub> H <sub>3</sub> , 4-MeC <sub>6</sub> H <sub>4</sub> )
<b>VIIIc</b>	1640	1670	1750	1.13 s (3H, Me); 1.28 t and 2.72 q (5H, CH <sub>2</sub> CH <sub>3</sub> ); 1.50 m, 1.62 m, and 3.15–3.50 m (10H, C <sub>5</sub> H <sub>10</sub> N); 3.87 s (1H, CH); 7.12 d, 7.30 d, 7.53 d, 7.71 d, and 7.82 s (7H, C <sub>6</sub> H <sub>3</sub> , 4-EtC <sub>6</sub> H <sub>4</sub> )
<b>VIIIId</b>	1640	1660	1740	1.10 s (3H, Me), 3.10–3.60 m (8H, C <sub>4</sub> H <sub>8</sub> NO), 4.07 s (1H, 7b-H), 7.22 d (1H, 4-H, <i>J</i> = 8.8), 7.53 m (2H, <i>m</i> -H), 7.60 m (1H, <i>p</i> -H), 7.62 d.d (1H, 5-H, <i>J</i> = 8.8, 2.5), 7.78 m (2H, <i>o</i> -H), 7.89 d (1H, 7-H, <i>J</i> = 2.5)
<b>VIIIe</b>	1640	1660	1750	1.17 s (3H, Me); 1.29 t and 2.73 q (5H, CH <sub>2</sub> CH <sub>3</sub> ); 3.15–3.65 m (8H, C <sub>4</sub> H <sub>8</sub> NO); 3.92 s (1H, CH); 7.10 d, 7.31 d, 7.53 d, 7.71 d, and 7.78 s (7H, C <sub>6</sub> H <sub>3</sub> , 4-EtC <sub>6</sub> H <sub>4</sub> )
<b>VIIIIf</b>	1640	1660	1740	0.45 t, 1.12 m, and 2.16 m (5H, CH <sub>2</sub> CH <sub>3</sub> ); 3.15–3.65 m (8H, C <sub>4</sub> H <sub>8</sub> NO); 3.90 s (1H, CH); 7.10 d, 7.45–7.60 m, and 7.83 m (8H, C <sub>6</sub> H <sub>3</sub> , Ph)

1a,7b-dihydrocyclopropa[*c*]chromen-2-ones **VIIIId–VIIIIf** (Scheme 2, Table 1). The presence of a fused benzene ring in molecule **IX** did not hamper its reaction with zinc enolate **IIa** according to analogous scheme through intermediate **X**. The product was 1-benzoyl-1-methyl-1a-morpholinocarbonyl-1a,9c-dihydro-1*H*-3-oxacyclopropa[*c*]phenanthren-2-one (**XI**) (see Experimental).

The structure of compounds **VIIIa–VIIIIf** was proved by the IR and  $^1\text{H}$  NMR spectra. In the IR spectra of **VIIIa–VIIIIf**, absorption bands characteristic of the amide, aroyle, and lactone carbonyl groups were

present at 1640, 1660–1670, and 1740–1750  $\text{cm}^{-1}$ , respectively. The  $^1\text{H}$  NMR spectra of **VIIIa–VIIIe** contained signals at  $\delta$  3.86–3.96 and 1.13–1.17 ppm, which belong to the 7b-H proton and 1-CH<sub>3</sub> group, respectively; compound **VIIIIf** displayed signals at  $\delta$  0.45, 1.12, and 2.16 ppm, and singlets from 9c-H and 1-CH<sub>3</sub> appeared in the spectrum of **XI** at  $\delta$  4.35 and 1.12 ppm, respectively. The  $^1\text{H}$  NMR data indicated that products **VIIIa–VIIIIf** and **XI** were isolated as a single stereoisomer. Judging by the intensity of additional minor signals, the fraction of the other isomer was less than 5%.

In order to obtain additional proofs for the product structure we analyzed the  $^{13}\text{C}$  NMR spectrum of 1-benzoyl-6-bromo-1-methyl-1a-morpholinocarbonyl-1a,7b-dihydrocyclopropa[*c*]chromen-2-one (**VIIIId**).



The spectrum was consistent with the assumed structure (see Experimental). The signals were assigned using a combination of two-dimensional correlation techniques, HSQC and HMBC. Resonance signals at  $\delta_{\text{C}}$  32.06, 36.76, and 42.91 ppm belong to the  $\text{C}^{7\text{b}}$ ,  $\text{C}^{1\text{a}}$ , and  $\text{C}^1$  atoms, respectively, and indicate the presence of a cyclopropane fragment. The steric configuration of the latter was determined using NOE experiments, both two-dimensional (2D ROESY) and one-dimensional (difference NOE). Saturation of the 7b-H signal gave a positive nuclear Overhauser effect on 7-H ( $\eta_{\text{NOE}} = 10\%$ ), while the intensity of the methyl proton signal remained unchanged ( $\eta = 0$ ). No response was observed on the 7b-H signal upon saturation of the 1- $\text{CH}_3$  signal, but the intensity of the *o*-H signal increased ( $\eta_{\text{NOE}} \approx 5\%$ ). These data correspond to *trans* arrangement of the 7b-H proton and 1- $\text{CH}_3$  group in molecule **VIIIId**. Taking into account that the  $^1\text{H}$  NMR spectral patterns of compounds **VIIIa–VIIIc**, **VIIIe**, and **VIIIf** (Table 2) were similar to that observed for **VIIIId**, they were assigned analogous configuration.

## EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrometer from samples dispersed in mineral oil. The  $^1\text{H}$  NMR spectra of compounds **Va–Ve**, **Vg**, **VIIIa–VIIIc**, **VIIIe**, **VIIIf**, and **XI** were measured from solutions in  $\text{DMSO}-d_6$ - $\text{CCl}_4$  (1:3) using a Bruker DRX-500 instrument (500 MHz). The  $^{13}\text{C}$  NMR spectra of **Vf** and **VIIIId** were obtained on a Bruker DRX-400 spectrometer (100 MHz) using  $\text{DMSO}-d_6$  as solvent. Tetramethylsilane was used as internal reference. One- and two-dimensional NMR experiments were performed with solutions of compounds **Vf** and **VIIIId** in  $\text{DMSO}-d_6$  on a Bruker DRX-400 instrument (400 MHz for  $^1\text{H}$  and 100 MHz for  $^{13}\text{C}$ ).

**1-Alkyl-1-aryl-1a-acyl-1a,9c-dihydro-1H-3-oxa-cyclopropa[*c*]phenanthren-2-ones Va–Vg (general procedure).** A solution of 0.012 mol of 1-aryl-2,2-dibromoalkanone **Ia–Id** in 3 ml of ethyl acetate was added dropwise with stirring to a mixture of 3 g of fine zinc turnings, 8 ml of diethyl ether, and 5 ml of ethyl acetate. The mixture was heated until a reaction started, and the reaction then occurred spontaneously. When the reaction was complete, the mixture was heated for 15 min on a water bath and cooled, and the solution was separated by decanting. 2-Acyl-3H-benzo[*f*]chromen-3-one, 0.0075 mol, and HMPA, 2–4 ml, were added to the solution, 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  $\text{Na}_2\text{SO}_4$ , the solvent was distilled off, and the residue was recrystallized from methanol or toluene.

**1-Benzoyl-1a-(2-furoyl)-1-methyl-1a,9c-dihydro-1H-3-oxacyclopropa[*c*]phenanthren-2-one (Vf).**  $^{13}\text{C}$  NMR spectrum,  $\delta_{\text{C}}$ , ppm (100 MHz): 13.60 ( $\text{CH}_3$ ), 30.19 ( $\text{C}^{9\text{c}}$ ), 35.91 ( $\text{C}^{1\text{a}}$ ), 44.83 ( $\text{C}^1$ ), 109.56 ( $\text{C}^{9\text{b}}$ ), 113.36 ( $\text{C}^4$ ), 116.79 ( $\text{C}^4$ ), 119.58 ( $\text{C}^3$ ), 123.26 ( $\text{C}^9$ ), 126.04 ( $\text{C}^7$ ), 128.02 ( $\text{C}^8$ ), 128.52 ( $\text{C}^m$ ), 128.68 ( $\text{C}^6$ ), 128.94 ( $\text{C}^o$ ), 130.21 ( $\text{C}^5$ ), 130.69 ( $\text{C}^{5\text{a}}$ ), 131.27 ( $\text{C}^{9\text{a}}$ ), 132.82 ( $\text{C}^p$ ), 136.19 ( $\text{C}^i$ ), 147.96 ( $\text{C}^{3\text{a}}$ ), 149.04 ( $\text{C}^5$ ), 150.19 ( $\text{C}^{2\text{i}}$ ), 161.25 ( $\text{C}^2$ ), 178.33 (1a-C=O), 196.20 (1-C=O).

**1-Alkyl-1-aryl-6-bromo-1a-piperidinocarbonyl-1a,7b-dihydrocyclopropa[*c*]chromen-2-ones VIIIa–VIIIc and 1-alkyl-1-aryl-6-bromo-1a-morpholinocarbonyl-1a,7b-dihydrocyclopropa[*c*]chromen-2-ones VIIIId–VIIIf.** 1-Aryl-2,2-dibromoalkanone, 0.015 mol, was added to a mixture of 4 g of fine zinc turnings, 7 ml of diethyl ether, and 10 ml of ethyl acetate. The mixture was heated until a reaction started, and the reaction then occurred spontaneously. When the reaction was complete, the mixture was heated for 15 min on a water bath and cooled, and the solution was separated by decanting. Compound **VIa** or **VIb**, 0.01 mol, was then added, and the mixture was heated for 30–40 min under reflux, cooled, treated with 5% hydrochloric acid, and extracted. The solvent was distilled off from the extract, and the product was recrystallized from acetone or methanol.

**1-Benzoyl-6-bromo-1-methyl-1a-morpholinocarbonyl-1a,7b-dihydrocyclopropa[*c*]chromen-2-one (VIIIId).**  $^{13}\text{C}$  NMR spectrum ( $\text{DMSO}-d_6$ ),  $\delta_{\text{C}}$ , ppm: 13.33 (Me), 32.06 ( $\text{C}^{7\text{b}}$ ), 36.76 ( $\text{C}^{1\text{a}}$ ), 42.36 ( $\text{NCH}_2$ ), 42.91 ( $\text{C}^1$ ), 46.24 ( $\text{NCH}_2$ ), 65.35 and 65.69 ( $2\text{OCH}_2$ ),

117.25 (C<sup>6</sup>), 118.47 (C<sup>7a</sup>), 118.92 (C<sup>4</sup>), 128.07 (C<sup>m</sup>), 129.10 (C<sup>o</sup>), 132.33 (C<sup>p</sup>), 132.26 (C<sup>5</sup>), 132.33 (C<sup>7</sup>), 137.01 (C<sup>i</sup>), 149.01 (C<sup>3a</sup>), 160.51 (C<sup>2</sup>), 161.95 (1a-C=O), 197.30 (1-C=O).

**1-Benzoyl-1-methyl-1a-morpholinocarbonyl-1a,9c-dihydro-1H-3-oxacyclopropa[c]phenanthren-2-one (XI)** was synthesized in a similar way from compound **IX**; the product was recrystallized from acetone. Yield 2.5 g (56%), mp 221–223°C. IR spectrum,  $\nu$ , cm<sup>-1</sup>: 1640 (C=O, amide), 1660 (C=O, ketone), 1740 (C=O, lactone). <sup>1</sup>H NMR spectrum (500 MHz, DMSO-*d*<sub>6</sub>-CCl<sub>4</sub>, 1:3),  $\delta$ , ppm: 1.13 s (3H,

Me), 3.25–3.6 m (8H, C<sub>4</sub>H<sub>8</sub>NO), 4.35 s (1H, CH), 7.3–8.2 m (11H, C<sub>10</sub>H<sub>6</sub>, C<sub>6</sub>H<sub>5</sub>).

This study was performed under financial support by the Russian Foundation for Basic Research (project no. 04-03-96036).

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