*Russian Journal of General Chemistry, Vol. 74, No. 6, 2004, pp. 937–938. Translated from Zhurnal Obshchei Khimii, Vol. 74, No. 6, 2004, pp. 1013–1014.*


# Reactions of Zinc Enolates of Substituted 1-Aryl-2,2-dibromobutanones with Alkyl Esters of 3-Oxo-3*H*-benzo[*f*]chromene-2-carboxylic Acid

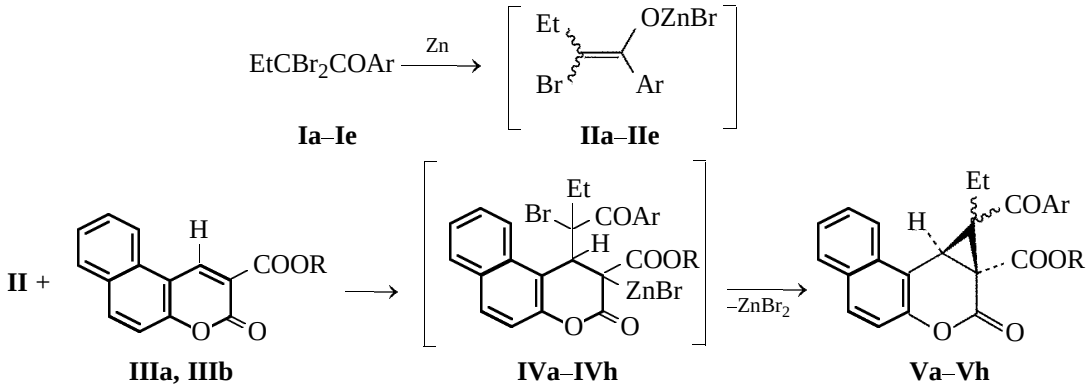
**V. V. Shchepin, N. Yu. Russkikh, M. M. Kalyuzhnyi, R. V. Shchepin, and M. I. Vakhrin**

*Perm State University, Perm, Russia*

Received June 4, 2002

**Abstract** — Zinc enolates derived from substituted 1-aryl-2,2-dibromobutanones react with alkyl 3-oxo-3*H*-benzo[*f*]chromene-2-carboxylates to form alkyl 1-aroyl-1-ethyl-2-oxo-1,9*c*-dihydro-3-oxacyclopropa[*c*]-phenanthrene-1*a*-carboxylate as a single geometric isomer.

In the preceding short communication we reported that bromine-containing zinc enolates derived from substituted α,α-dibromobutyrophenones add by the double bond of methyl 6-bromo-2-oxochromene-2-carboxylate [1]. In the present work we studied the ability of these zinc enolates to react with alkyl 3-oxo-3*H*-benzo[*f*]chromene-2-carboxylate (**III**). It was shown that zinc enolates **IIa**–**IIe** obtained from *para*-substituted 1-aryl-2,2-dibromobutanones **Ia**–**Ie** regiospecifically add to the double bond of substrates **IIIa**, **IIIb** to form intermediates **IVa**–**IVh** by the following scheme.




**I, II**, Ar = Ph (**a**), 4-$MeC_6H_4$ (**b**), 4-$FC_6H_4$ (**c**), 4-$ClC_6H_4$ (**d**), 4-$BrC_6H_4$ (**e**). **III**, R = Me (**a**), Et (**b**). **IV, V**, R = Me, Ar = Ph (**a**), 4-$MeC_6H_4$ (**b**), 4-$FC_6H_4$ (**c**), 4-$ClC_6H_4$ (**d**), 4-$BrC_6H_4$ (**e**); R = Et, Ar = Ph (**f**), 4-$ClC_6H_4$ (**g**), 4-$BrC_6H_4$ (**h**).

Intermediates **IVa**–**IVh** undergo a spontaneous stereospecific cyclization to give alkyl 1-aroyl-1-ethyl-2-oxo-1,9*c*-dihydro-3-oxocyclopropa[*c*]phenanthrene-1*a*-carboxylates **Va**–**Vh** in high yields (see table).

The composition and structure of compounds **Va**–**Vh** were proved by their elemental analysis and $^1$H and IR spectroscopy. The IR spectra contain characteristic absorption bands at 1675–1680, 1720, and 1755–1760 $cm^{-1}$, belonging to aroyl, ester, and lactone carbonyls. The $^1$H NMR spectra display characteristic signals at 4.03–4.10 ppm, s (CH), as well as alkoxycarbonyl and ethyl proton signals (see table). The aromatic protons absorb at 7.00–8.40 ppm. In particular, the methine proton gives a single singlet, implying that the products are formed as a single geometric isomer.

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Yields, melting points, $^1$H NMR spectra, and elemental analyses of alkyl 1-aroyl-1-ethyl-2-oxo-1,9*c*-dihydro-3-oxacyclopropa[*c*]phenanthrene-1*a*-carboxylates **Va**–**Vh**

| Comp. no | Yield, % | mp, °C | Solvent | $^1$H NMR spectrum, δ, ppm | | | Found, % | | Formula | Calculated, % | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | CH | COOR | Et | C | H | | C | H |
| **Va** | 82 | 207–209 | $CDCl_3$ | 4.03 s | 3.50 s ($CH_3$) | ~0.70–1.40, ~1.70–2.40 m ($CH_2$), 0.33 t ($CH_3$) | 74.82 | 4.95 | $C_{25}H_{20}O_5$ | 74.99 | 5.03 |
| **Vb** | 85 | 212–213 | $CDCl_3$ | 4.03 s | 3.50 s ($CH_3$) | ~0.70–1.40, ~1.70–2.40 m ($CH_2$), 0.33 t ($CH_3$) | 75.43 | 5.26 | $C_{26}H_{22}O_5$ | 75.53 | 5.35 |
| **Vc** | 79 | 193–195 | DMSO-$d_6$ | 4.04 s | 3.43 s ($CH_3$) | ~0.70–2.30 m ($CH_2$), 0.33 t ($CH_3$) | 71.60 | 4.50 | $C_{25}H_{19}FO_5$ | 71.76 | 4.58 |
| **Vd** | 83 | 240–242 | DMSO-$d_6$ | 4.10 s | 3.47 s ($CH_3$) | ~0.65–1.35, ~1.60–2.35 m ($CH_2$), 0.27 t ($CH_3$) | 68.89 | 4.32 | $C_{25}H_{19}ClO_5$ | 69.05 | 4.40 |
| **Ve** | 70 | 257–259 | $CDCl_3$ | 4.03 s | 3.47 s ($CH_3$) | ~0.70–1.40, ~1.60–2.30 m ($CH_2$), 0.23 t ($CH_3$) | 62.60 | 3.97 | $C_{25}H_{19}BrO_5$ | 62.64 | 3.99 |
| **Vf** | 80 | 191–192 | $CDCl_3$ | 4.07 s | 3.98 q ($CH_2$), 0.94 t ($CH_3$) | ~0.70–1.40, ~1.65–2.40 m ($CH_2$), 0.34 t ($CH_3$) | 75.22 | 5.30 | $C_{26}H_{22}O_5$ | 75.35 | 5.35 |
| **Vg** | 82 | 214–216 | $CDCl_3$ | 4.06 s | 4.00 q ($CH_2$), 1.00 t ($CH_3$) | ~0.75–1.45, ~1.65–2.40 m ($CH_2$), 0.37 t ($CH_3$) | 69.40 | 4.65 | $C_{26}H_{21}ClO_5$ | 69.56 | 4.72 |
| **Vh** | 71 | 222–223 | $CDCl_3$ | 4.04 s | 3.99 q ($CH_2$), 1.00 t ($CH_3$) | ~0.75–1.45, ~1.65–2.40 m ($CH_2$), 0.34 t ($CH_3$) | 63.21 | 4.23 | $C_{26}H_{21}BrO_5$ | 63.30 | 4.29 |

## EXPERIMENTAL

The IR spectra were measured on a UR-20 spectrophotometer in mineral oil. The $^1$H NMR spectra were recorded in $CDCl_3$ and DMSO-$d_6$ on an RYa-2310 instrument (60 MHz), internal reference HMDS.

**Alkyl 1-aroyl-1-ethyl-2-oxo-1,9*c*-dihydro-3-oxacyclopropa[*c*]phenanthrene-1*a*-carboxylates Va–Vh.** A solution of 0.016 mol of 1-aryl-2,2-dibromobutanone **Ia**–**Ie** in 3 ml of ethyl acetate was added dropwise to 3 g of fine zinc turnings in 8 ml of ether and 5 ml of ethyl acetate. The mixture was heated until reaction began and then occurred spontaneously. After the reaction was complete, the mixture was heated for 20 min on a water bath, cooled, decanted from zinc into another flask, and a solution of 0.008 mol of compound **IIIa**, **IIIb** in 2–5 ml of HMPA was added to it. The resulting mixture was refluxed for 30 min, cooled, hydrolyzed with 5% HCl, extracted with diethyl ether, dried with $Na_2SO_4$, the solvent was removed, and the reaction product was recrystallized from toluene–methanol.

## REFERENCES

1. Shchepin, V.V., Kalyuzhnyi, M.M., and Shchepin P.V., *Khim. Geterotsikl. Soedin.*, 2001, no. 10, p. 1415.