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Reaction of Zinc Enolates Derived from Substituted 2,2-Dibromobutyrophenones with Ethyl 5,5-Dimethyl-2-oxo-2,5-dihydrofuran-3-carboxylate

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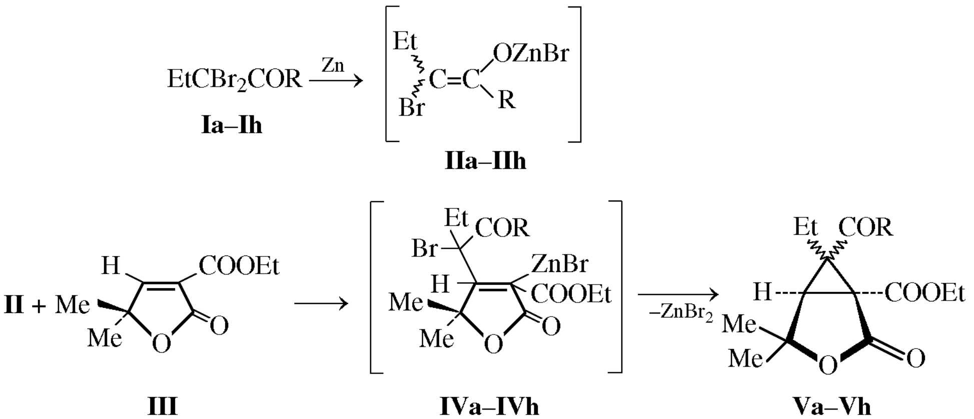
Abstract—Zinc enolates derived from substituted 2,2-dibromobutyrophenones react with ethyl 5,5-dimethyl-2-oxo-2,5-dihydrofuran-3-carboxylate to give ethyl 6-aroyl-6-ethyl-4,4-dimethyl-2-oxo-3-oxabicyclo[3.1.0]hexane-1-carboxylates mostly as a single geometric isomer.

Earlier we found that zinc enolates derived from α,α-dibromoketones very actively react by the carbonyl group of aldehydes and ketones to produce compounds of various classes, such as α,β-unsaturated ketones, α,β-epoxyketones, and β-diketones [1, 2].

In the present work we studied synthetic potential of these zinc enolates in reactions with compounds with activated C=C bonds on an example of ethyl 5,5-dimethyl-2-oxo-2,5-dihydrofuran-3-carboxylate. It was found that zinc enolates **IIa**–**IIh** obtained from *para*-substituted 2,2-dibromobutyrophenones **Ia**–**Ih** add to the double bond of compound **III**.

Under the reaction conditions, intermediates **IVa**–**IVh** undergo cyclization to give bicyclic products, ethyl 6-aroyl-6-ethyl-4,4-dimethyl-2-oxo-3-oxabicyclo[3.1.0]hexane-1-carboxylates **Va**–**Vh** in high yields (see table).



R = Ph (**a**), 4-MeC_6H_4 (**b**), 4-EtC_6H_4 (**c**), 4-*t*-BuC_6H_4 (**d**), 4-FC_6H_4 (**e**), 4-ClC_6H_4 (**f**), 4-BrC_6H_4 (**g**), 4-$C_6H_5C_6H_4$ (**h**).

The structure of compounds **Va**–**Vh** was confirmed by the elemental analyses and ^1H NMR and IR spectra. The IR spectra contain typical absorption bands of the aroyl (1680–1690 cm^{-1}), ethoxycarbonyl (1730–1740 cm^{-1}), and lactone carbonyls (1785–1790 cm^{-1}). The ^1H NMR spectra show signals of the methine (2.48–2.56 and 4.29–4.35 ppm), ethoxycarbonyl (1.28–1.36 and 1.60–2.30 ppm), and CMe_2 protons (0.82–0.90 and 1.33–1.47 ppm). The ^1H NMR data suggest that compounds **Va**–**Ve** and **Vg** are formed as single geometric isomers. At the same time, the spectra of compounds **Vf** and **Vh** display, in addition to signals belonging to the major geometric isomer, a singlet signal at 3.80–3.83 ppm (other signals are hard

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Yields, constants, ^{1}H NMR spectra, and elemental analyses of ethyl 6-aroyl-6-ethyl-4,4-dimethyl-2-oxo-3-oxabicyclo-[3.1.0]hexane-1-carboxylates

Comp. no.	Yield, %	mp, °C	^{1}H NMR spectrum, δ, ppm					Found, %		Formula	Calculated, %	
			CH	COOEt	Et	CMe_2	COAr	C	H		C	H
Va	67	104–105	2.48 s	4.32 q, 1.33 t	1.83 q, 0.89 t	1.40 s, 1.38 s	7.87–8.15 m, 7.25–7.56 m (Ph)	68.90	6.63	$C_{19}H_{22}O_5$	69.08	6.71
Vb	85	159–160	2.53 s	4.29 q, 1.30 t	1.60–2.30 m, 0.82 t	1.40 s, 1.33 s	7.90 d, 7.18 d, 2.30 s (4-MeC_6H_4)	69.68	6.95	$C_{20}H_{24}O_5$	69.75	7.02
Vc	80	97–98	2.51 s	4.34 q, 1.32 t	1.60–2.30 m, 0.89 t	1.39 s, 1.33 s	7.97 d, 7.23 d, 2.64 q, 1.20 t (4-EtC_6H_4)	70.28	7.25	$C_{21}H_{26}O_5$	70.37	7.31
Vd	74	110–111	2.50 s	4.32 q, 1.32 t	1.82 q, 0.88 t,	1.38 s, 1.35 s	8.03 d, 7.44 d, 1.23 s (4-*t*-BuC_6H_4)	71.33	7.76	$C_{23}H_{30}O_5$	71.48	7.82
Ve	71	106–107	2.56 s	4.35 q, 1.36 t	1.90 q, 0.90 t,	1.47 s, 1.42 s	8.00–8.30 m, 6.90–7.30 m (4-FC_6H_4)	65.33	7.99	$C_{19}H_{21}FO_5$	65.51	6.08
Vf	72	140–141	2.51 s	4.33 q, 1.33 t	1.84 q, 0.85 t,	1.42 s, 1.38 s	8.07 d, 7.40 d (4-ClC_6H_4)	62.40	5.71	$C_{19}H_{21}ClO_5$	62.55	5.80
Vg	76	146–147	2.50 s	4.30 q, 1.28 t	1.80 q, 0.83 t,	1.37 s, 1.34 s	7.92 d, 7.57 d (4-BrC_6H_4)	55.59	5.07	$C_{19}H_{21}BrO_5$	55.76	5.17
Vh	78	173–174	2.53 s	4.31 q, 1.33 t	1.90 q, 0.88 t,	1.40 s, 1.37 s	8.17 d, 7.25–7.70 m (4-$C_6H_5C_6H_4$)	73.12	6.32	$C_{25}H_{26}O_5$	73.87	6.45

to identify), which indicates that the other geometric isomer is present in smaller amounts. The ratio between the major and minor isomers is ca. 90 : 10%. To summarize, assuming that compounds **Va**–**Vh** are formed as the least strained bicycles, the above structure seems to be the most probable.

EXPERIMENTAL

The IR spectra were taken on a UR-20 spectrophotometer for pure compounds. The ^{1}H NMR spectra were measured for $CDCl_3$ solutions on an RYa-2310 instrument (60 MHz) against internal HMDS.

Ethyl 5,5-dimethyl-2-oxo-2,5-dihydrofuran-3-carboxylate was prepared by the procedure described in [3].

Ethyl 6-aroyl-6-ethyl-4,4-dimethyl-3-oxabicyclo[3.1.0]hexane-1-carboxylates Va–Vh. To 5 g of zinc in the form of small chips in 10 ml of ether and 10 ml of ethyl acetate, 0.015 mol of compound **Ia**–**Ih** in 10 ml of ethyl acetate was added dropwise with stirring. The mixture was heated to initiate a self-sustaining reaction. After the reaction had been complete, the mixture was heated for 15 min on a water bath, cooled, and decanted from zinc into another flask. Then 0.01 mol of compound **III** was added, the mixture was heated for 30 min on a water bath, cooled, hydrolyzed with 5% HCl, and extracted with ether. The extract was dried with Na_2SO_4, the solvents were distilled off, and the products were recrystallized from methanol.

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