

Reactions of 1-Aryl-2,2-dibromobutan-1-ones with Zinc and Alkyl 6-Bromo-2-oxo-2-*H*-chromen-3-carboxylate

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Received July 27, 2001

Abstract— Zinc enolates formed from 1-aryl-2,2-dibromobutan-1-ones and zinc react with alkyl 6-bromo-2-oxo-2-*H*-chromen-3-carboxylates affording alkyl 1-aryl-6-bromo-2-oxo-1-ethyl-1,7b-dihydrocyclopropa[*c*]-chromen-1a(2*H*)-carboxylates as a single isomer.

In extension of the study on reactivity of halogenated zinc enolates with respect to activated double bond [1] we investigated the reaction of zinc enolates **IIa-h** obtained from 1-aryl-2,2-dibromobutan-1-ones **Ia-h** and zinc with alkyl 6-bromo-2-oxo-2-*H*-chromen-3-carboxylates (**IIIa-c**). The results of experiments show that zinc enolates **IIa-h** attack by their C-nucleophilic center the electron-deficient C⁴ carbon of compounds **IIIa-c** furnishing addition products, intermediates **IVa-j**. The latter in ether-ethyl acetate solution spontaneously undergo cyclization into the final products, alkyl 1-aryl-6-bromo-2-oxo-1-ethyl-1,7b-dihydrocyclopropa[*c*]chromen-1a(2*H*)-carboxylates (**Va-j**) along the following scheme.

The structure of compounds **Va-j** was proved by elemental analysis, ¹H NMR and IR spectra.

In the IR spectra of compounds obtained are present characteristic absorption bands of stretching vibrations of C=O bond in aryl (1685–1695 cm⁻¹), methoxycarbonyl (1730–1740 cm⁻¹), and lactone groups (1765–1775 cm⁻¹).

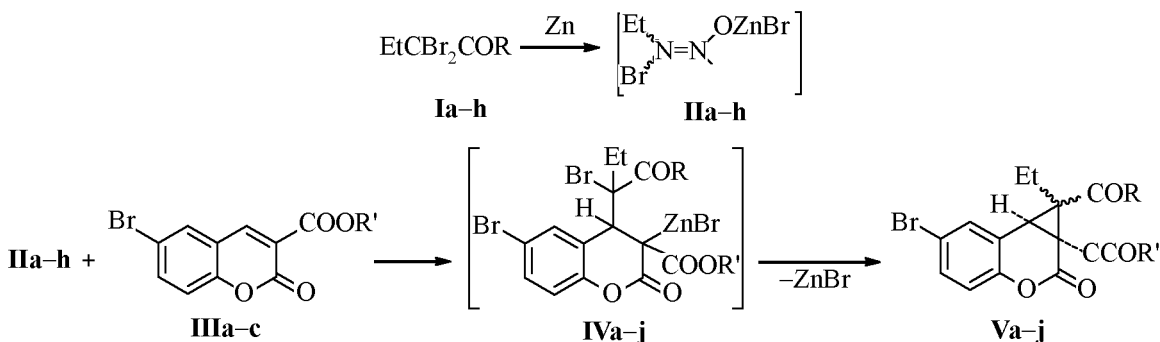
In the ¹H NMR spectra appear characteristic signals in the regions 3.52–3.63, 1.50–2.50, 0.70–1.60, 0.45–0.53 ppm corresponding to methine proton and to protons of ethyl group.

The ¹H NMR data evidence that compounds **Va-j** form as a single geometric isomer. It is also presumable that the compounds synthesized have the least strained structure with the eclipsed position of hydrogen atoms attached to C^{7b} and to C^{1a} in the alkoxy-carbonyl group.

EXPERIMENTAL

IR spectra of individual compounds were recorded on spectrophotometer UR-20. ¹H NMR spectra from solutions of compounds in CDCl₃ and DMSO-*d*₆ were registered on spectrometer RYa-2310 (60MHz), internal reference HMDS. Alkyl 6-bromo-2-oxo-2-*H*-chromen-3-carboxylates (**III**) were prepared by procedure [2].

Alkyl 1-aryl-6-bromo-2-oxo-1-ethyl-1,7b-dihydrocyclopropa[*c*]chromen-1a(2*H*)-carboxylates



I, II, R = Ph (**a**), 4-MeC₆H₄ (**b**), 4-EtC₆H₄ (**c**), 4-*t*-BuC₆H₄ (**d**), 4-FC₆H₄ (**e**), 4-ClC₆H₄ (**f**), 4-BrC₆H₄ (**g**), 4-PhC₆H₄ (**h**); **III**, R' = Me (**a**), Et (**b**), Me₂CHCH₂CH₂ (**c**); **IV, V**, R' = Me, R = Ph (**a**), 4-MeC₆H₄ (**b**), 4-EtC₆H₄ (**c**), 4-*t*-BuC₆H₄ (**d**), 4-FC₆H₄ (**e**), 4-ClC₆H₄ (**f**), 4-BrC₆H₄ (**g**), 4-PhC₆H₄ (**h**); R = Et, R = Ph (**i**); R' = Me₂CHCH₂CH₂, R = 4-BrC₆H₄ (**j**).

Table 1. Yields, melting points, and elemental analyses of alkyl 1-*aroyl*-6-bromo-2-oxo-1-ethyl-1,7*b*-dihydrocyclopropa[*c*]chromen-1*a*(2*H*)-carboxylates **Va–j**

Compd. no.	Yield, %	mp, °C	Found, %		Formula	Calculated, %	
			C	H		C	H
Va 52	170–171	58.60	3.84	C ₂₁ H ₁₇ BrO ₅	58.76	3.99	
Vb	34	196–197	59.50	4.23	C ₂₂ H ₁₉ BrO ₅	59.61	4.32
Vc	50	173–174	60.32	4.50	C ₂₃ H ₂₁ BrO ₅	60.41	4.63
Vd	53	196–197	61.72	5.06	C ₂₅ H ₂₅ BrO ₅	61.87	5.19
Ve	60	197–198	56.28	3.46	C ₂₁ H ₁₆ BrFO ₅	56.40	3.61
Vf	65	228–230	53.80	3.38	C ₂₁ H ₁₆ BrClO ₅	54.39	3.48
Vg	66	235–237	49.51	3.04	C ₂₁ H ₁₆ Br ₂ O ₅	49.64	3.17
Vh	64	241–242	64.01	4.10	C ₂₇ H ₂₁ BrO ₅	64.17	4.19
Vi	67	150–152	59.50	4.27	C ₂₂ H ₁₉ BrO ₅	59.61	4.32
Vj	65	153–155	53.10	4.18	C ₂₅ H ₂₄ Br ₂ O ₅	53.22	4.29

Table 2. IR and ¹H NMR spectra of compounds **Va–j**

Compd. no.	IR spectrum, ν, cm ⁻¹			¹ H NMR spectrum, δ, ppm ^a
	C=O ketone	C=O ester	C=O lactone	
Va	1685	1740–1765		0.45 t (3H, CH ₃), 1.50–2.30 m (2H, CH ₂), 3.40 s (3H, OCH ₃), 3.68 s (1H, CH), 6.90–8.00 m (8H, C ₆ H ₃ , C ₆ H ₅)
Vb	1690	1730	1770	0.53 t (3H, CH ₃), 0.80–1.60 m, 1.60–2.40 m (2H, CH ₂), 2.35 s (3H, CH ₃ C ₆ H ₄), 3.48 s (3H, OCH ₃), 3.58 s (1H, CH), 6.80–8.00 m (7H, C ₆ H ₃ , 4-CH ₃ C ₆ H ₄)
Vc	1690	1730	1765	0.50 t (3H, CH ₃), 0.80–1.60 m, 1.60–2.40 m (2H, CH ₂), 1.16 t (3H, CH ₃ CH ₂ C ₆ H ₄), 2.62 q (2H, CH ₃ CH ₂ C ₆ H ₄), 3.40 s (3H, OCH ₃), 3.60 s (1H, CH), 6.80–8.00 m (7H, C ₆ H ₃ , 4-C ₂ H ₅ C ₆ H ₄)
Vd	1690	1740	1775	0.44 t (3H, CH ₃), 0.70–1.50 m, 1.50–2.40 m (2H, CH ₂), 1.14 s (9H, C(CH ₃) ₃), 3.40 s (3H, OCH ₃), 3.68 s (1H, CH), 6.80–8.00 m (7H, C ₆ H ₃ , (CH ₃) ₃ CC ₆ H ₄)
Ve	1685	1730	1770	0.53 t (3H, CH ₃), 0.80–1.60 m, 1.60–2.40 m (2H, CH ₂), 3.47 s (3H, OCH ₃), 3.54 s (1H, CH), 6.70–8.10 m (7H, C ₆ H ₃ , 4-FC ₆ H ₄)
Vf	1695	1730	1770	0.47 t (3H, CH ₃), 0.70–1.50 m, 1.50–2.30 m (2H, CH ₂), 3.40 s (3H, OCH ₃), 3.63 s (1H, CH), 6.90–8.00 m (7H, C ₆ H ₃ , 4-ClC ₆ H ₄)
Vg	1690	1740	1770	0.45 t (3H, CH ₃), 0.70–1.50 m, 1.50–2.30 m (2H, CH ₂), 3.40 s (3H, OCH ₃), 3.66 s (1H, CH), 6.90–8.00 m (7H, C ₆ H ₃ , 4-BrC ₆ H ₄)
Vh	1690	1740	1765	0.50 t (3H, CH ₃), 0.70–1.50 m, 1.50–2.30 m (2H, CH ₂), 3.40 s (3H, OCH ₃), 3.63 s (1H, CH), 6.90–8.00 m (12H, C ₆ H ₃ , 4-C ₆ H ₅ C ₆ H ₄)
Vi	1690	1730	1770	0.50 t (3H, CH ₃), 0.70–1.50 m, 1.50–2.30 m (2H, CH ₂), 0.90 t (3H, OCH ₂ CH ₃), 3.52 s (1H, CH), 3.83 q (2H, OCH ₂ CH ₃), 6.70–8.00 m (8H, C ₆ H ₃ , C ₆ H ₅)
Vj	1695	1730	1770	0.45 t (3H, CH ₃), 0.60–1.50 m, 3.84 t (11H, CH ₂ CH ₂ CH(CH ₃) ₂), 0.70–1.50 m, 1.50–2.30 m (2H, CH ₂), 3.60 s (1H, CH), 6.80–8.00 m (7H, 4-BrC ₆ H ₄)

^a ¹H NMR spectra of compounds **Va, c, d, f–h, j** were registered in DMSO-*d*₆, of compounds **Vb, e, i** in CDCl₃.

(Va-j) (see Tables 1, 2). To 5 g of finely dispersed zinc in 10 ml of ether and 10 ml of ethyl acetate was added dropwise at stirring a solution of 0.017 mol of 1-aryl-2,2-dibromobutan-1-one in 10 ml of ethyl acetate. The mixture was heated till the reaction started, and then it continued spontaneously. On completion of the reaction the mixture was heated for 15 min on a water bath, then it was cooled and decanted from zinc into another flask. Then to this solution was added 0.01 mol of compound **III**, the mixture was boiled for 30 min, cooled, hydrolyz-

ed with 5% HCl, the reaction products were extracted into ether, and the extracts were dried on Na₂SO₄, the solvents were distilled off, and the products were recrystallized from benzene-hexane mixture.

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