

Reactions of Zinc Enolates Derived from 1-Aryl-2,2-dibromoalkanones with 3-Acetyl-6-bromochromen-2-one

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Received June 4, 2002

Abstract—Zinc enolates derived from substituted 1-aryl-2,2-dibromoalkanones react with 3-acetyl-6-bromochromen-2-one to give 1a-acetyl-1-alkyl-1-aroyle-6-bromo-1a,7b-dihydro-1*H*-cyclopropa[*c*]chromen-2-ones as a single stereoisomer.

While developing a general procedure for cyclopropanation of heterocyclic compounds with simultaneous introduction of an aroyl group [1, 2], we have examined the reaction of 3-acetyl-6-bromochromen-2-one with bromine-containing zinc enolates **IIa–IIg** obtained from 1-aryl-2,2-dibromoalkanones **Ia–Ig**. The reaction follows Scheme 1. Zinc enolates **IIa–IIg** regioselectively add at the C³=C⁴ double bond of 3-acetyl-6-bromochromen-2-one to give intermediates **IIIa–IIIg** which undergo stereoselective cyclization, affording the final products, 1a-acetyl-1-alkyl-1-aroyle-6-bromo-1a,7b-dihydro-1*H*-cyclopropa[*c*]chromen-2-ones **IVa–IVg** as a single stereoisomer (see table).

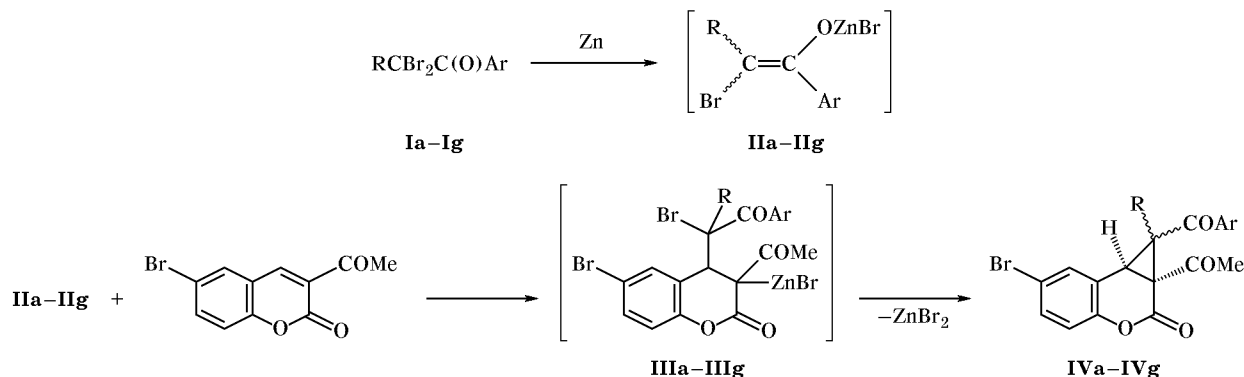
The structure of compounds **IVa–IVg** was proved by elemental analysis and IR and ¹H NMR spectroscopy. Their IR spectra contained characteristic absorp-

tion bands from the carbonyl groups at about 1675 (COAr), 1700 (COMe), and 1750 cm⁻¹ [C²=O]. In the ¹H NMR spectra we observed singlets in the regions δ 3.57–3.65 and 2.33–2.50 ppm, which belong to the 7b-H and 1a-acetyl protons, respectively. The presence of only one set of signals in the ¹H NMR spectrum of each compound **IVa–IVg** indicates that only one stereoisomer is formed.

EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrometer from samples dispersed in mineral oil. The ¹H NMR spectra were obtained on an RYa-2310 instrument (60 MHz) from solutions in CDCl₃ or DMSO-*d*₆ using HMDS as internal reference.

Scheme 1.



I–IV, R = Me, Ar = 4-ClC₆H₄ (**a**), 4-BrC₆H₄ (**b**); R = Et; Ar = Ph (**c**), 4-MeC₆H₄ (**d**), 4-FC₆H₄ (**e**), 4-ClC₆H₄ (**f**), 4-BrC₆H₄ (**g**).

Yields, melting points, ^1H NMR spectra, and elemental analyses of 1a-acetyl-1-alkyl-1-aroyle-6-bromo-1a,7b-dihydro-1H-cyclopropa[c]chromen-2-ones **IVa–IVg**

Comp. no.	Yield, %	mp, °C	^1H NMR spectrum, ^a δ , ppm			Naideno, %		Formula	Calculated, %	
			CH	COMe	R	C	H		C	H
IVa	64	211–213	3.60 s	2.38 s	1.17 s	55.24	3.19	$\text{C}_{20}\text{H}_{14}\text{BrClO}_4$	55.39	3.35
IVb	65	230–231	3.65 s	2.33 s	1.10 s	50.10	2.87	$\text{C}_{20}\text{H}_{14}\text{Br}_2\text{O}_4$	50.24	2.95
IVc	63	184–185	3.60 s	2.50 s	~0.85–2.30 m (CH_2), 0.63 t (CH_3)	61.10	4.05	$\text{C}_{21}\text{H}_{17}\text{BrO}_4$	61.03	4.15
IVd	67	202–203	3.63 s	2.45 s	~0.85–2.30 m (CH_2), 0.63 t (CH_3)	61.71	4.38	$\text{C}_{22}\text{H}_{19}\text{BrO}_4$	61.84	4.48
IVe	69	201–203	3.58 s	2.43 s	~0.85–2.30 m (CH_2), 0.60 t (CH_3)	58.37	3.70	$\text{C}_{21}\text{H}_{16}\text{BrFO}_4$	58.49	3.74
IVf	65	223–225	3.67 s	2.38 s	~0.85–2.30 m (CH_2), 0.53 t (CH_3)	56.28	3.54	$\text{C}_{21}\text{H}_{16}\text{BrClO}_4$	56.34	3.60
IVg	63	209–211	3.57 s	2.39 s	~0.85–2.30 m (CH_2), 0.57 t (CH_3)	51.17	3.22	$\text{C}_{21}\text{H}_{16}\text{Br}_2\text{O}_4$	51.25	3.28

^a Solvents: $\text{DMSO}-d_6$ (**IVb**, **IVf**), CDCl_3 (**IVc**, **IVd**), $\text{DMSO}-d_6$ - CDCl_3 (1:1) (**IVa**, **IVe**, **IVg**).

1a-Acetyl-1-alkyl-1-aroyle-6-bromo-1a,7b-dihydro-1H-cyclopropa[c]chromen-2-ones IVa–IVg.

A solution of 0.012 mol of 1-aryl-2,2-dibromoalkane **Ia–Ig** in 3 ml of ethyl acetate was added dropwise with stirring to a mixture of 3 g of fine zinc turnings, 8 ml of ether, and 5 ml of ethyl acetate. The mixture was heated until a reaction started, and the process continued spontaneously. When the reaction was complete, the mixture was heated for 15 min on a water bath and cooled, and the solution was separated from the remaining zinc by decanting into another flask. 3-Acetyl-6-bromochromen-2-one, 0.0075 mol, and HMPA, 2–4 ml, were added, and

the mixture was heated for 30 min on a water bath, cooled, treated with 5% hydrochloric acid, and extracted with ether. The extract was dried over sodium sulfate and evaporated, and the residue was recrystallized from methanol or toluene.

REFERENCES

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