

SHORT
COMMUNICATIONS

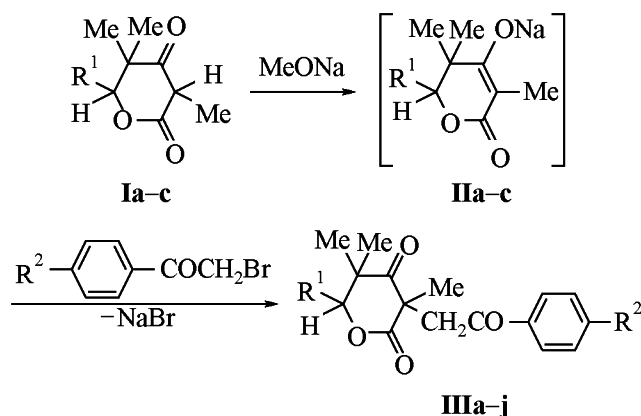
Alkylation with Substituted Phenacyl
Bromides of Sodium Enolates
from 6-Aryl-3,5,5-trimethyl-2,3,5,6-tetrahydropyran-2,4-diones

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We have established formerly that reaction of ethyl 2,4-dibromo-2,4-dimethyl-3-oxopentanoate with zinc and aromatic aldehydes gives rise to previously unknown 6-aryl-3,5,5-trimethyl-2,3,5,6-tetrahydropyran-2,4-diones [1]. It is known that tetrahydropyran-2,4-diones with substituents in 3-position containing a carbonyl group possess various kinds of biological activity [2-4]. Aiming at preparation of new tetrahydropyran-2,4-diones types with aroylmethyl group in 3-position of the pyran ring we studied reactions between sodium enolates (**II**) obtained from 6-aryl-3,5,5-trimethyl-2,3,5,6-tetrahydropyran-2,4-diones (**I**) and *para*-substituted phenacyl bromides. The investigation established that the reaction between these compounds occurred readily in anhydrous DMSO yielding C-alkylation products of sodium enolates **IIa-c**, 6-aryl-3-aroymethyl-3,5,5-trimethyl-2,3,5,6-tetrahydropyran-2,4-diones (**IIIa-j**).



I, II, R¹ = Ph (**a**), 4-ClC₆H₄ (**b**), 4-BrC₆H₄ (**c**); **III**,
R¹ = Ph: R² = Br (**a**), NO₂ (**b**); R¹ = 4-ClC₆H₄:
R² = Br (**c**), NO₂ (**d**); R¹ = 4-BrC₆H₄: R² = Et (**e**),
t-Bu (**f**), F (**g**), Br (**h**), NO₂ (**i**), Ph (**j**).

Yields of synthesized compounds **IIIa-j** amount to 60-79%. The composition and the structure of compounds **IIIa-j** were proved by elemental analysis, IR and ¹H NMR spectroscopy. In the IR spectra are observed the characteristic absorption bands of carbonyl groups around 1680 (COAr), 1715 (CO), 1750 cm⁻¹ (COO). In the ¹H NMR spectra appear characteristic singlets in the 0.97-1.13, 1.50-1.63, 6.00-6.17 ppm region belonging respectively to the protons of methyl groups (CMe₂, Me), and to methine proton. Also is present a doublet of doublets from the protons of CH₂ group at 3.77-4.03 ppm with a coupling constant *J* 18 Hz. A single set of proton resonances for each of compounds obtained evidences the formation of a single geometrical isomer.

6-Aryl-3-aroymethyl-3,5,5-trimethyl-2,3,5,6-tetrahydropyran-2,4-diones (IIIa-j). A dry sodium methylate obtained from 0.03 mol of Na and 10 ml of MeOH was dissolved in 15 ml of DMSO, and 0.02 mol of 6-aryl-3,5,5-trimethyl-2,3,5,6-tetrahydropyran-2,4-dione was added thereto. Methyl alcohol was distilled off under reduced pressure of a water-jet pump, and to residual solution was added 0.02 mol of substituted phenacyl bromide, the reaction mixture was stirred at 30-40°C for 30 min, and then it was poured into water. The separated precipitate was filtered off and recrystallized from acetone.

¹H NMR spectra, yields, melting points, and elemental analyses are presented in Tables 1 and 2.

¹H NMR spectra of compounds solutions in CDCl₃ were registered on spectrometer RYa-2310 (60 MHz), internal reference HMDS. IR spectra were

Table 1. ¹H NMR spectra of 6-Aryl-3-arylmethyl-3,5,5-trimethyl-2,3,5,6-tetrahydropyran-2,4-diones **IIIa-j**, δ, ppm

Compd. no.	CMe ₂	CH ₃	CH	R ¹	CH ₂ (<i>J</i> 18 Hz)	4-R ² -C ₆ H ₄ CO
IIIa	1.00 s, 1.03 s	1.53 s	6.10 s	7.31 s (Ph)	3.77 d, 3.93 d	7.47 d, 7.73 d (4-BrC ₆ H ₄)
IIIb	1.07 s, 1.13 s	1.63 s	6.13 s	7.40 s (Ph)	3.83 d, 4.03 d	8.03 d, 8.33 d (4-NO ₂ C ₆ H ₄)
IIIc	1.03 s, 1.07 s	1.57 s	6.17 s	7.38 s (4-ClC ₆ H ₄)	3.83 d, 4.00 d	7.57 d, 7.80 d (4-BrC ₆ H ₄)
III d	1.03 s, 1.08 s	1.57 s	6.07 s	7.33 s (4-ClC ₆ H ₄)	3.83 d, 4.00 d	8.00 d, 8.27 d (4-NO ₂ C ₆ H ₄)
IIIe	1.00 s	1.55 s	6.13 s	7.32 d, 7.47 d (4-BrC ₆ H ₄)	3.77 d, 3.97 d	1.15 t, 2.63 k (Et), 7.18 d, 7.80 d (4-EtC ₆ H ₄)
III f	1.03 s	1.57 s	6.17 s	7.30 d, 7.47 d (4-BrC ₆ H ₄)	3.80 d, 3.97 d	1.20 s (<i>t</i> -Bu), 7.37 d, 7.83 d (4- <i>t</i> -BuC ₆ H ₄)
III g	0.97 s	1.50 s	6.10 s	7.27 d, 7.43 d (4-BrC ₆ H ₄)	3.77 d, 3.93 d	6.77–7.33 m, 7.67–8.08 m (4-FC ₆ H ₄)
III h	1.03 s, 1.07 s	1.57 s	6.13 s	7.37 d, 7.60 d (4-BrC ₆ H ₄)	3.80 d, 3.97 d	7.27 d, 7.77 d (4-BrC ₆ H ₄)
III i	0.97 s, 1.02 s	1.53 s	6.00 s	7.20 d, 7.47 d (4-BrC ₆ H ₄)	3.77 d, 3.97 d	7.93 d, 8.20 d (4-NO ₂ C ₆ H ₄)
III j	1.00 s	1.55 s	6.13 s	7.08–7.67 m (4-BrC ₆ H ₄)	3.77 d, 4.00 d	7.60 d, 7.93 d, 7.08–7.67 m (4-C ₆ H ₅ -C ₆ H ₄)

Table 2. Yields, melting points, and elemental analyses of 6-aryl-3-arylmethyl-3,5,5-trimethyl-2,3,5,6-tetrahydropyran-2,4-diones **IIIa-j**

Compd. no.	Yield, %	mp, °C	Found, %		Formula	Calculated, %	
			C	H		C	H
IIIa	65	186–187	61.44	4.82	C ₂₂ H ₂₁ BrO ₄	61.54	4.90
IIIb	62	227–228	66.75	5.29	C ₂₂ H ₂₁ NO ₆	66.84	5.32
IIIc	69	213–215	56.87	4.27	C ₂₂ H ₂₀ BrClO ₄	56.96	4.31
III d	72	223–226	61.35	4.61	C ₂₂ H ₂₀ ClNO ₆	61.47	4.66
IIIe	63	150–151	62.94	5.42	C ₂₄ H ₂₅ BrO ₄	63.02	5.47
III f	60	182–183	64.20	5.90	C ₂₆ H ₂₉ BrO ₄	64.33	5.98
III g	75	209–212	58.99	4.43	C ₂₂ H ₂₀ BrFO ₄	59.06	4.47
III h	79	211–213	51.87	3.89	C ₂₂ H ₂₀ Br ₂ O ₄	51.97	3.94
III i	77	226–227	55.61	4.18	C ₂₂ H ₂₀ BrNO ₆	55.70	4.22
III j	71	202–204	66.41	4.90	C ₂₈ H ₂₅ BrO ₄	66.53	4.95

recorded on spectrometer UR-20 from mulls in mineral oil.

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