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Synthesis of arylidene derivatives of *N*-unsubstituted pyrrolin-2-ones

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5-Alkyl(aryl)-3-arylidene-3*H*-pyrrolin-2-ones were synthesized by ammonolysis of their *O*-heteroanalogs or by the reactions of 5-alkyl(aryl)-3*H*-pyrrolin-2-ones with aromatic aldehydes. The structures of the compounds obtained were confirmed by ^{1}H NMR spectra.

Key words: *N*-nonsubstituted 5-alkyl(aryl)-3*H*-pyrrolin-2-ones, 5-alkyl(aryl)-3-arylidene-3*H*-furan-2-ones, 5-alkyl(aryl)-3-arylidene-3*H*-pyrrolin-2-ones, aromatic aldehydes, 4-oxoalkanoic acids, ammonolysis, condensation.

There are many examples of the condensation of aromatic aldehydes with 5*H*-furan-2-ones**[1,2]** and 3*H*-furan-2-ones.**[3,4]** At the same time, the reactions of aromatic aldehydes with their nitrogen-containing analogs, namely, 3*H*-pyrrolin-2-ones, have been described only for 1-alkyl-5-aryl-3*H*-pyrrolin-2-ones**[5]** since 5-alkyl-3*H*-pyrrolin-2-ones are not easily accessible.

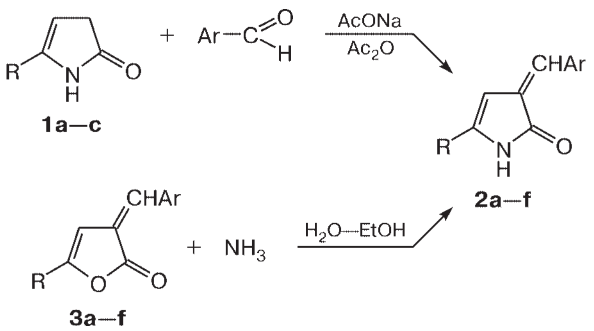
Heterocyclization of 4-oxoalkanoic acids under the action of ammonium acetate afforded *N*-nonsubstituted 5-alkyl(aryl)-3*H*-pyrrolin-2-ones (**1**) in good yields.**[6]**

In the present work, the condensation of compounds **1a—c** with aldehydes of the benzene and furan series was studied.

Results and Discussion

Reactions were carried out in acetic anhydride in the presence of anhydrous sodium acetate (Scheme 1).

Scheme 1



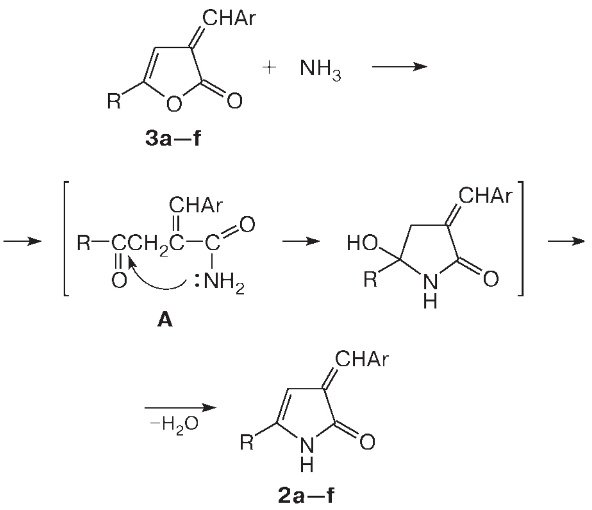
	a	**b**	**c**	**d**	**e**	**f**
R	*n*-C_5H_{11}	*n*-C_7H_{15}	Ph	Ph	Ph	*n*-C_5H_{11}
Ar	Ph	Ph	Ph	2-HOC_6H_4	3-$NO_2C_6H_4$	2-HOC_6H_4

The reactions proceed slowly, and the yields of the final products do not exceed 30%, probably, because of a side acylation involving the nitrogen atom of the heterocycle.

To increase the yield of arylidene derivatives **2a—f**, we started from 5-alkyl(aryl)-3-arylidene-3*H*-furan-2-ones **3a—f**, which already contain an arylidene substituent at the C(3) atom of the heterocycle. Compounds **3** were prepared by condensation of aromatic aldehydes with 4-oxoalkanoic acids according to our previous procedure.**[7]**

Compounds **3a—f** were refluxed with a threefold excess of ammonia in aqueous ethanol (Scheme 2). The yields of the target products were 75—85%.

Scheme 2



Apparently, the ammonolysis of arylidenefuranones **3a—f** causes the opening of the furan ring, and the resulting substituted 4-oxoalkanamides undergo *in situ* cycliza-

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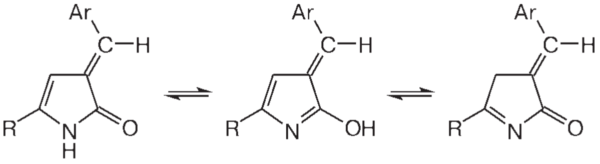
tion into 5-alkyl(aryl)-3-arylidene-3*H*-pyrrolin-2-ones **2a—f**; however, intermediate **A** was not isolated.

Arylidene derivatives **2a—f** can exist as three tautomers.



I II III

The IR spectra of compounds **2a—c** contain absorption bands at 1730—1710 cm^{-1} from the carbonyl group of unsaturated lactams and the absorption bands of the double bond of the heterocycle and the exocyclic C=C bond at 1630—1620 and 1670—1650 cm^{-1}, respectively, and shows no band of the OH group, which enables one to exclude tautomer II for these compounds. The ^{1}H NMR data indicate that compounds **2a—e** predominantly exist as form I. Their spectra contain a singlet at δ 6.40—6.70 for the vinyl H(4) protons of the heterocycle. The position of a signal for the proton at the exocyclic sp^2-C atom is determined by the withdrawing ability of the aryl substituent, and these signals appear at δ 6.60—7.10. In the ^{1}H NMR spectra of compounds **2a,b**, a series of highfield signals at δ –0.85 to 2.05 was assigned to the 5-alkyl substituent.

Experimental

IR spectra were recorded on an IKS-29 instrument (Vaseline oil). ^{1}H NMR spectra were recorded on a Varian FT-80A instrument (80 MHz) in $CDCl_3$ with Me_4Si as the internal standard. Chemical shifts are given on the δ scale. The yields and characteristics of the compounds obtained are presented in Tables 1 and 2.

Table 1. Physicochemical characteristics of the compounds synthesized

Compound	M.p. /°C	Yield* (%)	Found/Calculated (%) C	H	N	Molecular formula
2a	215—216	26 (*A*)	79.51	7.76	5.92	$C_{16}H_{19}NO$
		62 (*B*)	79.66	7.88	5.81	
2b	219—220	18 (*A*)	79.63	9.20	5.31	$C_{18}H_{23}NO$
		57 (*B*)	80.26	8.61	5.20	
2c	165—166	28 (*A*)	82.73	5.38	6.19	$C_{17}H_{13}NO$
		85 (*B*)	82.59	5.26	5.66	
2d	190—191	30 (*A*)	77.39	5.33	4.80	$C_{17}H_{13}NO_2$
		92 (*B*)	77.56	4.94	5.32	
2e	>225 decomp.	28 (*A*)	69.52	4.56	9.90	$C_{17}H_{12}N_2O_3$
		68 (*B*)	69.86	4.11	9.59	
2f	205—206	30 (*A*)	74.46	7.42	5.56	$C_{16}H_{19}NO_2$
		90 (*B*)	74.71	7.39	5.45	

* The methods are referred to in parentheses.

Table 2. ^{1}H NMR spectra of 5-R-3-arylidene-3*H*-pyrrolin-2-ones **2a—e**

Compound	δ				
	(s, 1 H, H(4))	(s, 1 H, =CH—Ar)	R	Ar	NH
2a	6.40	6.60	0.85—1.95	7.10—7.40	8.00
2b	6.49	6.70	0.85—2.05	7.10—7.40	8.00
2c	6.60	6.80	—	7.10—7.50	8.00
3a	6.55	6.65	—	7.10—7.50	8.05
3b	6.70	7.10	—	7.20—7.50	8.00
3c	6.50	6.70	0.85—1.90	7.10—7.48	8.05

5-Alkyl(aryl)-3-arylidene-3*H*-furan-2-ones and 5-alkyl(aryl)-3*H*-pyrrolin-2-ones were prepared as described in Refs. 7 and 8, respectively.

5-Alkyl(aryl)-3-arylidene-3*H*-pyrrolin-2-ones 2a—f. *A*. From 5-aryl-3*H*-pyrrolin-2-ones 1a—c. A mixture of compounds **1a—c** (0.3 mol) and an aromatic aldehyde (0.3 mol) was heated with freshly melted sodium acetate (0.3 mol) in acetic anhydride (1.2 mol) at 70—80 °C. The reaction mixture was cooled and poured into ice, and the crystals that formed were separated and recrystallized from isopropyl alcohol—chloroform.

***B*. From 5-alkyl(aryl)-3-arylidene-3*H*-furan-2-ones 3a—f.** A 25% solution of ammonia in aqueous ethanol (20 mL) was added to compounds **3a—f** (0.3 mol), and the reaction mixture was refluxed for 30 min. Another portion of ammonia in aqueous ethanol (20 mL) was added, and refluxing was continued for an additional 30 min. Then K_2CO_3 (2 g) was added, and the reaction mixture was refluxed for 1 h with gradual addition of a solution of ammonia (20 mL) and cooled. The crystals that formed were filtered off, washed with water, and recrystallized from isopropyl alcohol—chloroform.

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