AMINOMETHYLATION OF SOME 4-THIAZOLIDINONES

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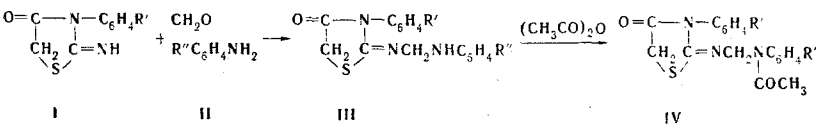
2-Arylaminomethylimino-3-aryl-4-oxothiazolidines were obtained by the Mannich reaction. The structure of the isolated products was confirmed by acid hydrolysis, the formation of monoacetyl derivatives, and the IR spectra.

The aminomethylation of 2-imino-3-aryl-4-oxothiazolidines had not been studied until we began our present research. It is known that rhodanine and its 5-substituted derivatives undergo the Mannich reaction in the 3 position of the thiazolidine ring [1, 2]. 2-Imino-3-aryl-4-oxothiazolidines I react readily with formaldehyde and primary aromatic amines IIb to give aminomethyl derivatives in high yields. Compounds I, which have two labile hydrogen atoms, can undergo the Mannich reaction at both the imino and methylene groups. On the basis of a study of the IR spectra and the products of the acid hydrolysis, it was established that the condensation of I proceeds at the imino group and that the products have the IIIa-m structure (Table 1).



I II III IV

An intense absorption band is observed in the region of the stretching vibrations of the carbonyl group of III at 1710-1720 cm^{-1}; this is characteristic for the stretching vibrations of an unconjugated carbonyl group [3]. The structure of III is confirmed by the presence in the IR spectrum of intense absorption bands at 1630 and 1470 cm^{-1} due to the stretching vibrations of the C=N and CH_2 groups [4]. In contrast to starting I, the absorption at 3300 cm^{-1} corresponding to the stretching vibrations of the NH group is absent in the IR spectra of products III; this is in agreement with the proposed structure of the compounds.

TABLE 1. 2-Arylaminomethylimino-3-aryl-4-oxothiazolidines

Compound	R′	R″	mp, °C	Empirical formula	Found, %			Calc., %			Yield, %
					N, %	S, %	M	N, %	S, %	M	
IIIa	H	H	118—119	$C_{16}H_{15}N_3OS$	14,3	10,6	290	14,1	10,8	297	92
IIIb	p-CH_3	H	133—134	$C_{17}H_{17}N_3OS$	13,6	9,9	306	13,5	10,0	311	90
IIIc	p-CH_3O	H	150—151	$C_{17}H_{17}N_3O_2S$	12,9	9,7	320	12,8	9,8	327	88
IIId	H	p-CH_3	143—144	$C_{17}H_{17}N_3OS$	13,6	10,2	303	13,5	10,2	311	93
IIIe	p-CH_3	p-CH_3	151—152	$C_{18}H_{19}N_3OS$	13,1	9,9	316	12,9	9,8	325	91
IIIf	p-CH_3O	p-CH_3	130—131	$C_{18}H_{19}N_3O_2S$	12,5	9,3	337	12,3	9,4	341	90
IIIg	p-C_2H_5O	p-CH_3	151—152	$C_{19}H_{21}N_3O_2S$	11,9	8,9	350	11,8	9,0	355	87
IIIh	H	p-Br	187—188	$C_{16}H_{14}BrN_3OS$	11,8	8,5	371	11,2	8,5	376	89
IIIi	p-CH_3	p-Br	174—175	$C_{17}H_{16}BrN_3OS$	10,7	8,2	379	10,8	8,2	389	86
IIIj	p-CH_3O	p-Br	152—153	$C_{17}H_{16}BrN_3O_2S$	10,5	7,8	396	10,3	7,9	405	85
IIIk	p-C_2H_5O	p-Br	162—163	$C_{18}H_{18}BrN_3O_2S$	10,6	7,6	413	10,0	7,6	419	80
IIIl	*m*-NO_2	H	204—205	$C_{16}H_{14}N_4O_3S$	16,5	9,3	335	16,4	9,3	342	84
IIIm	p-CH_3	*m*-NO_2	193—194	$C_{17}H_{16}N_4O_3S$	15,9	8,9	350	15,7	9,0	356	82

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TABLE 2. 2-Acetylarylaminomethylimino-3-aryl-4-oxothiazolidines

Compound	R′	R″	mp, °C (from alcohol)	Empirical formula	N, % found	N, % calc.	Yield, %
IVa	H	p-CH_3	187—188	$C_{15}H_{19}N_3O_2S$	11,8	11,9	86
IVb	p-CH_3	*m*-NO_2	158—159	$C_{19}H_{18}N_4O_4S$	14,2	14,1	80
IVc	p-OCH_3	H	167—168	$C_{19}H_{19}N_3O_3S$	11,2	11,4	84
IVd	p-OCH_3	p-CH_3	119—120	$C_{20}H_{21}N_3O_3S$	10,8	10,9	89
IVe	p-CH_3	p-Br	164—165	$C_{19}H_{18}BrN_3O_2S$	9,6	9,7	92
IVf	p-OC_2H_5	p-Br	142—143	$C_{20}H_{20}BrN_3O_3S$	9,2	9,1	87

Mannich bases III are stable in dilute acid solutions at 20°C but are readily hydrolyzed on brief heating to 3-aryl-2,4-thiazolidinediones and the starting amines. The acetylation of III with acetic anhydride proceeds upon simple mixing of the components; the products are 2-acetylarylaminomethylimino-3-aryl-4-oxothiazolidines IVa-f (Table 2).

EXPERIMENTAL

The IR spectra of KBr pellets at 600-3600 cm^{-1} were recorded with a UR-20 spectrometer. The molecular weights were determined from the mass spectra recorded with an MKh-1303 mass spectrometer at an inlet-system and ion-source temperature of 250°, an ionizing voltage of 50 V, emission current of 1.5 mA, and accelerating voltage of 2 kV. The 2-imino-3-aryl-4-oxothiazolidines (I) were obtained by reaction of acetochloroacetic anhydride with arylthioureas [5].

2-Phenylaminomethylimino-3-phenyl-4-oxothiazolidine (IIIa). A 2.5 ml sample of 36% formalin and 0.6 g of aniline were added at 0° to a solution of 1.5 g of 2-imino-3-phenyl-4-oxothiazolidine in 40 ml of ethanol. After 1 h, the precipitate was removed by filtration, washed with water, and dried. The other III were synthesized under similar conditions.

Acid Hydrolysis. A 1 g sample of IIIa was refluxed for 5 min in 25 ml of 10% HCl, after which the mixture was cooled, and the precipitate was removed by filtration to give a product with mp 143-144° (from alcohol) in 43% yield. No melting-point depression was observed for a mixture of this product with an authentic sample of 3-phenyl-2,4-thiazolidinedione [5]. The filtrate was neutralized with 10% Na_2CO_3 solution, saturated with alkali, and extracted with ether. The amine contained in the ether extract was treated with a mixture of acetic anhydride and acetic acid. The resulting acetanilide (26%) had mp 114°.

Acid Hydrolysis of IVd. Water (0.5 g), 0.5 g of CH_3COOH, and 1 g of acetic anhydride were added to 0.5 g of IVd. The crystals that formed were removed by filtration after 1 h.

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