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BRIEF COMMUNICATIONS

Efficient Synthesis of 3-Acyl-5-arylmethylene-4-oxothiazolidine-2-thiones

E. B. Aronova and A. I. Ginak

St. Petersburg State Technological Institute, St. Petersburg, Russia

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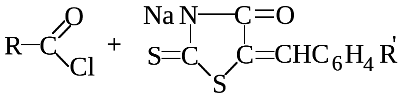
Abstract—An efficient procedure was suggested for preparing 3-acyl-5-arylmethylene-4-oxothiazolidine-2-thiones.

3-Acyl-5-arylmethylene-4-oxothiazolidine-2-thiones are intermediates in synthesis of practically important substances: pesticides, drugs, dyes, vulcanizing agents, antioxidants, etc. [1]. These compounds are prepared in solutions by reactions of appropriate acyl chlorides with 5-arylmethylene-4-oxothiazolidine-2-thiones in the presence of bases [2, 3]. The reactions are accompanied by hydrolysis with ring cleavage, which decreases the yield of the target products by 25–40% and complicates their isolation from reaction mixtures. Synthesis of 3-acyl-5-arylmethylene-4-oxothiazolidine-2-thiones by cyclization from appropriate amides and carbon disulfide [4] is multistage and gives poor yields. Therefore, we suggest in this paper a procedure for preparing 3-acyl-5-arylmethylene-4-oxothiazolidine-2-thiones by direct acylation of solid alkali metal salts of 5-arylmethylene-4-oxothiazolidine-2-thiones with vapors of appropriate acyl chlorides (see table). It is known [5] that nucleophilic substitution reactions of solid ambident substrates with gaseous electrophiles are selective and are not complicated by degradation.

The reaction was performed in a tubular reactor (1 cm in diameter, 10 cm high) equipped with controllable (70–250°C) electric heating. Acyl chloride vapor mixed with an inert gas (nitrogen, argon) was passed through a substrate bed. The reaction progress was monitored by TLC. After reaction completion, excess acyl chloride was removed in a vacuum.

The acylation pathway was judged from the hydrolysis products. Addition of the acyl group to the nitrogen atom in the heterocycle follows from formation of the initial 5-arylmethylene-4-oxothiazolidine-2-thione in hydrolysis, according to the scheme



Yields after recrystallization Y, decomposition points T_{dec}, and elemental analyses of oxothiazolidinethiones **Ia**–**Ij**

Compound	Y, %	T_{dec}, °C	Found, %/Calculated, %		Formula
			N	S	
Ia	66.2	132–132.5	5.40/5.32	23.24/24.35	$C_{12}H_9NO_2S_2$
Ib	74.5	154–155	4.31/4.35	19.99/19.71	$C_{17}H_{11}NO_2S_2$
Ic	71.1	147–148	3.88/3.94	18.47/18.04	$C_{18}H_{13}NO_3S_2$
Id	72.8	137–138	4.04/4.08	19.48/18.68	$C_{17}H_{10}NO_2S_2F$
Ie	73.6	176–177	4.36/4.13	18.13/18.89	$C_{18}H_{13}NO_2S_2$
If	76.7	155–156	3.83/4.13	18.15/18.89	$C_{18}H_{13}NO_2S_2$
Ig	69.2	184–185	4.16/3.94	18.02/18.04	$C_{18}H_{13}NO_3S_2$
Ih	74.5	211–212	4.05/3.89	16.92/17.82	$C_{16}H_{10}NO_2S_2Cl$
Ii	67.2	219–220	7.97/7.60	17.97/17.40	$C_{19}H_{16}N_2O_2S_2$
Ij	68.1	215–216	7.12/7.56	17.01/17.31	$C_{17}H_{10}N_2O_4S_2$

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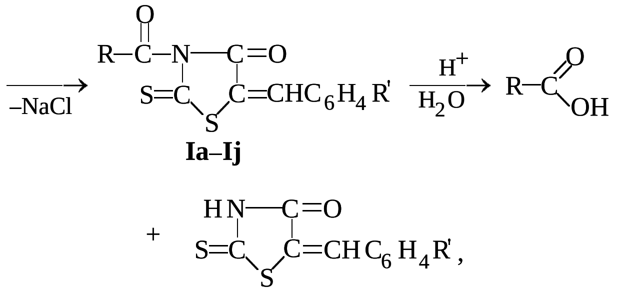

where R = Me, R' = H (**a**); R = Ph, R' = H (**b**); R = *p*-$CH_3OC_6H_4$, R' = H (**c**); R = *p*-FC_6H_4, R' = H (**d**); R = *p*-$CH_3C_6H_4$, R' = H (**e**); R = Ph, R' = *p*-CH_3 (**f**); R = Ph, R' = *p*-CH_3O (**g**); R = Ph, R' = *p*-Cl (**h**); R = Ph, R' = *p*-$N(CH_3)_2$ (**i**); and R = Ph, R' = *p*-NO_2 (**j**).

The structure of hydrolysis products was confirmed by independent synthesis [6] and TLC (Silufol UV-254, acetone–hexane–acetic acid, 1 : 2 : 0.01 [7]), and the structure of **Ia**–**Ij**, by coincidence of their UV and IR spectra with those of the known compounds [8].

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