A STUDY OF AZOLIDONES AND THEIR DERIVATIVES.

III.* The Synthesis and Certain Transformations of 4-Thioxo-5-alkylthiazolidones-2

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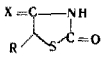
A study was made of the reaction of 5-alkylthiazolidindiones-2, 4 (I) with P_2S_5 in a medium of dioxane. 4-Thioxo-derivatives of compound I were obtained which readily react with ammonia and amines with the formation of 4-imino- and 4-arylimino-derivatives.

It is well known that the synthesis of various 4-substituted derivatives of thiazolidindione-2, 4 proceeds with difficulty because of the inert nature of the oxo group in position 4 [2]. Replacement of the oxygen atom by sulfur markedly activates this position and makes possible the synthesis of a number of new substances [3].



Compound	R	X	Mp °C (decomp.)	Empirical formula	Found, %		Calculated, %		Yield, %
					N	S	N	S	
II	CH_3	S	110*	$C_4H_5NOS_2$	9.3	43.3	9.5	43.5	55
III	C_2H_5	S	108*	$C_5H_7NOS_2$	8.9	39.9	8.6	39.7	60
IV	$(CH_3)_2CH$	S	83*	$C_6H_9NOS_2$	8.2	36.7	7.9	36.6	40
V	CH_3	C_6H_5N	190	$C_{10}H_{10}N_2OS$	13.8	15.0	13.5	15.5	40
VI	C_2H_5	C_6H_5N	174*	$C_{11}H_{12}N_2OS$	12.8	14.6	12.7	14.5	50
VII	$(CH_3)_2CH$	C_6H_5N	193	$C_{12}H_{14}N_2OS$	12.2	13.2	11.9	13.6	46
VIII	CH_3	Py—CONHN**	179*	$C_{10}H_{10}N_4O_2S$	22.5	13.0	22.3	12.8	50
IX	C_2H_5	Py—CONHN**	167*	$C_{11}H_{12}N_4O_2S$	21.2	12.1	21.2	12.1	48
X	$(CH_3)_2CH$	Py—CONHN**	175*	$C_{12}H_{14}N_4O_2S$	20.3	11,6	20.1	11.5	50
XI	CH_3	C_6H_5NHN	231*	$C_{10}H_{11}N_3OS$	19.3	14.5	19,0	14,5	64
XII	C_2H_5	C_6H_5NHN	131	$C_{11}H_{13}N_3OS$	17.7	13.3	17.8	13.6	74
XIII	$(CH_3)_2CH$	C_6H_5NHN	149*	$C_{12}H_{15}N_3OS$	16.9	12.9	16.8	12.8	62
XIV	CH_3	NH	194	$C_4H_6N_2OS$	21.3	24.2	21.5	24.6	48
XV	C_2H_5	NH	211	$C_5H_8N_2OS$	19.0	22.5	19.4	22.2	51
XVI	$(CH_3)_2CH$	NH	236—238	$C_6H_{10}N_2OS$	17.7	20.3	17.7	20.2	70
XVII	C_6H_5CH	NH	266	$C_{10}H_8N_2OS$	13.80	15.65	13.71	15.70	65
XVIII	α-$C_{10}H_7CH$	NH	248	$C_{14}H_{10}N_2OS$	11.28	12.45	11.02	12.61	70
XIX	3,4-$(OCH_3)_2C_6H_3CH$	NH	260	$C_{12}H_{12}N_2O_3S$	10.82	12.35	10.61	12.14	50

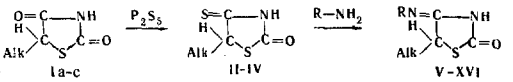
*Melt without decomposition

**Py, pyridyl-4

In the present work a study was made of the reaction in which 4-thioxo-5-alkylthiazolidones-2 (II–IV) are obtained and their conversion into 4-imino- and 4-aryliminoderivatives (V–XVI). During the interaction of compound I with P_2S_5 in a medium of dioxane, the 4-thioxoderivatives of compound I (II–IV) were obtained in which the thionyl group is distinguished by its enhanced activity. On heating compounds II–IV readily condense with amines and ammonia with the formation of the corresponding 4-iminoderivatives (V–XVI). The structure of the products formed on interaction with ammonia (XIV–XIX) was proved in the case of compound XIV by acid hydrolysis, during which the corresponding derivative of compound I is formed. Phenylhydrazine reacts with compound II–IV in the cold on mixing equimolar quantities of the original substances in methanol.

One should note that the presence of the arylidene residue in position 5 does not affect the activity of the sulfur atom in position 4. The 5-arylidene derivatives of isorhodanine [4] react with concentrated ammonia in an analogous manner to compound II with the formation of the corresponding 4-imino-5-arylidene derivatives of compound I (XVII–XIX.

*For part II, see [1].



EXPERIMENTAL

5-Alkylthiazolidindiones-2,4(Ia–Ic) were obtained according to a previously described method [5].

4-Thioxo-5-alkylthiazolidones-2 (II–IV) were obtained by boiling a mixture of 0.04 mole of 5-alkylthiazolidindione-2,4 (Ia–Ic), 0.014 mole of P_2S_5, and 10 ml of absolute dioxane for 4 hr. After boiling with active charcoal, the solution was filtered and the dioxane was distilled under vacuum. The dry residue was crystallized from water (yellow needles).

4-Imino-5-alkyl(arylidene)thiazolidones-2(V–X, XIV–XIX) A solution containing 0.01 mole of the corresponding thione (II–IV) and 0.01 mole of aniline or hydrazine of isonicotinic acid in 10 ml methanol was boiled for 1 hr. Compounds XIV–XIX are obtained by heating 0.01 mole of the corresponding thione with 6 ml of conc ammonia for 15 min in a boiling water bath. After cooling, the precipitate was removed by filtration and washed with water or methanol. The compound was crystallized from methanol or water (colorless crystals); compounds XVII and XIX were crystallized from acetic acid and compound XVIII was crystallized from dioxane.

4-Phenylhydrazones of 5-alkylthiazolidindiones (XI–XIII) were obtained in an analogous manner to compounds V–X, only the reactions proceeded at room temperature. Colorless needles crystallized out from methanol.

Acid hydrolysis of compound XIV. A 0.01 mole quantity of compound XIV and 5 ml of 5% HCl were boiled for 15 min, the mixture was cooled, and the precipitate was removed by filtration. After crystallization from water the melting point was 41° C without depression in a mixture with a known sample of 5-methylthiazolidindione-2,4 [5].

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