RESEARCH ON ARYLHYDRAZONES OF SUBSTITUTED GLYOXYLIC ACIDS.
XX*. CYCLIZATION OF ARYLHYDRAZONES OF CHLOROMETHYLGLYOXYLOYL CHLORIDE TO THIAZOLINE DERIVATIVES

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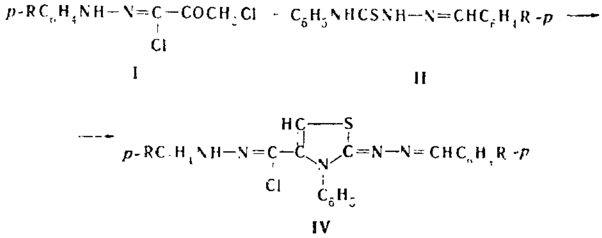
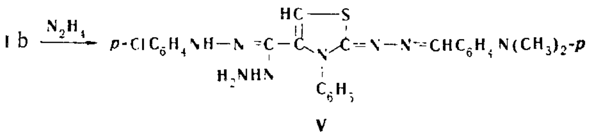
Substituted 2-benzalhydrazono-3-phenyl-4-(arylhydrazonochloroformyl)-4-thiazolines and 2,2'-azinobis[3-aryl-4-(arylhydrazonochloroformyl)-4-thiazolines], respectively, are formed in the condensation of arylhydrazones of chloromethylglyoxyloyl chloride with 4-phenylthiosemicarbazones and 1,6-diarylhydrazodithiocarbonamides.

The present paper is devoted to the synthesis of some new 2,3,4-substituted thiazolines, some of which are known to have biologically active properties [2, 3]. In order to achieve the synthesis, we used the previously synthesized [4] arylhydrazones of chloromethylglyoxyloyl chloride (I) as α-halocarbonyl compounds; I was subjected to the action of 4-phenylthiosemicarbazones (II) and 1,6-diarylhydrazodithiocarbonamides (III) [5-7]. In the first case, substituted 2-benzalhydrazono-3-phenyl-4-(arylhydrazonochloroformyl)-4-thiazolines (IV) (Table 1) were synthesized:



I a $R=H$; b $R=Cl$; c $R=NO_2$; d $R=CH_3$; IIa $R'=N(CH_3)_2$; b $R'=NO_2$; IVa $R=H$, $R'==N(CH_3)_2$; b $R=Cl$, $R'=N(CH_3)_2$; c $R=NO_2$, $R'=N(CH_3)_2$; d $R=H$, $R'=NO_2$; e $R=CH_3$, $R'=NO_2$.

In the case of Ib it was shown that the chloride atom, as in the arylhydrazones of glyoxyloyl chloride [8], is replaced by a hydrazine residue, as a result of which 2-(p-chlorophenylhydrazonohydrazinoformyl)-4-thiazoline (V, Table 1) is obtained:



Compounds I and III (in a ratio of 2:1) are cyclized to 2,2'-azinobis[3-aryl-4-(arylhydrazonochloroformyl)-4-thiazolines] (VI, Table 2).

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*See [1] for communication XIX.

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TABLE 1. Thiazolines IV-V

Compound	R	R′	mp, °C[a]	Empirical formula	N, % found	N, % calc.	Yield, %
IVa	H	N(CH$_3$)$_2$	114—115	$C_{25}H_{23}ClN_6S$	17,5	17,7	59
IVb	C*b*	N(CH$_3$)$_2$	155—156	$C_{25}H_{22}Cl_2N_6S$	16,3	16,5	55
IVc	NO$_2$	N(CH$_3$)$_2$	160—161	$C_{25}H_{22}ClN_7O_2S$	18,9	18,8	56
IVd	H	NO$_2$	166—167	$C_{23}H_{17}ClN_6O_2S$	17,4	17,6	52
IVe	CH$_3$[c]	NO$_2$	209—210	$C_{24}H_{19}ClN_6O_2S$	16,9	17,1	55
V	—	—	166—167[a]	$C_{25}H_{25}ClN_8S$	22,4	22,2	47

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a) From alcohol; b) Found: S 6.5%. Calculated: S 6.3%; c) Found S 6.6%. Calculated S 6.5%.

TABLE 2. Compounds VI

Compound	R	R′	mp, °C	Empirical formula	S, % found	S, % calc.	Yield, %
VIa	H	H	114—115	$C_{32}H_{24}Cl_2N_8S_2$	10,0	9,7	52
VIb	CH$_3$	H	167—168	$C_{34}H_{28}Cl_2N_8S_2$	9,6	9,4	54
VIc	CH$_3$	CH$_3$	177—178	$C_{36}H_{32}Cl_2N_8S_2$	8,8	9,0	53
VI[d]	CH$_3$*	C$_2$H$_5$O	174—175	$C_{38}H_{36}Cl_2N_8O_2S$	8,1	8,3	54

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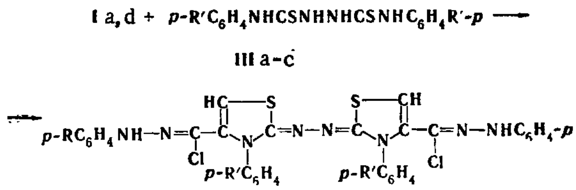
*Found: N 14.7%. Calculated: N 14.5%.



VI a-d

IIIa R′=H; b RR′=CH$_3$; c R′=OC$_2$H$_5$; VIa R=H, R′=H; b R=CH$_3$. R′=H; c R=CH$_3$, R′=CH$_3$; d R=CH$_3$, R′=OC$_2$H$_5$

The UV spectra of alcohol solutions of IV-VI contain two absorption maxima at 235-240 and 355-370 nm, which are close to the absorption maxima of the starting arylhydrazones of chloromethylglyoxyloyl chloride [4]. This demonstrates that the arylhydrazone grouping does not enter into conjugation with the thiazoline ring. Frequencies of vibrations at 1595-1610 (C=N), 3250 (NH) [9], 1330-1360, 1180-1260, 1010-1090, 935-960, and 830-860 cm^{-1}, which are characteristic for the thiazoline ring [10-12], are expressed distinctly in the IR spectra.

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EXPERIMENTAL

The IR spectra of KBr pellets (600-3600 cm^{-1}) were obtained with a UR-10 spectrometer. The UV spectra of $5 \cdot 10^{-5}$ M alcohol solutions of the compounds were recorded with an SF-4A spectrophotometer.

Compounds IV. Equimolecular mixture of I and II was refluxed in an alcohol solution for 12 h. The solution was cooled, and the resulting crystals were removed by filtration, washed with alcohol, and crystallized from alcohol. Information on IV is presented in Table 1.

Compounds VI. A mixture of 10 mmole of I and 5 mmole of III in 10 ml of absolute alcohol was refluxed for 12 h, after which the resulting precipitate was removed by filtration, washed with alcohol, and crystallized from alcohol. Information on VI is presented in Table 2.

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