SYNTHESIS OF 2-BENZAMIDOTHIAZOLINES

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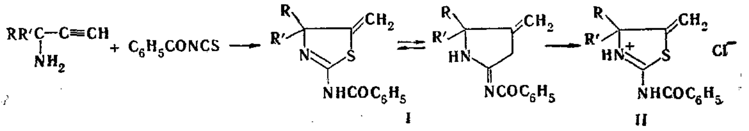
2-Benzamido-5-methylene-2-thiazolines were obtained by reaction of α-ethynylamines with benzoyl isothiocyanate. The resulting acylaminothiazolines have imino structures, while their hydrochlorides have amino structures.

In developing our research [1] involving a study of the reaction of acetylenic amines with isothiocyanates, we described the reaction of α-ethynylamines with acyl isothiocyanates, particularly with benzoyl isothiocyanate. Since acyl isothiocyanates are more reactive compounds than alkyl and aryl isothiocyanates, acetylenic amines react with benzoyl isothiocyanate more vigorously to give good yields of Ia-f (Table 1). The 2-benzamido-2-thiazolines are weak bases, and their hydrochlorides are hydrolyzed on dissolving in water.

Intramolecular cyclization at the triple bond to give a five-membered ring is confirmed by the PMR spectra: two doublets at 5.0-5.4 ppm with J = 1.5-2 Hz are characteristic for the nonequivalent geminal protons of an exocyclic methylene group (Table 2), the presence of which attests to the formation of a five-membered ring [2]. The absorption bands at 2100 and 3300 cm^{-1} that are characteristic for the $C \equiv C$ and $\equiv C-H$ stretching vibrations are absent in the IR spectra of Ia-f, but the spectra do contain absorption at 860-870 cm^{-1}, which also indicates the presence of an exocyclic methylene group [3].

Sheinker and co-workers [4, 5] have found that the introduction of electronegative substituents into the exocyclic nitrogen atom shift the tautomeric amine–imine equilibrium to favor predominance of the imine forms: in particular, the acyl derivatives of 2-aminothiazolines exist in the imine form in solution. An investigation of the IR spectra of crystals of the acylaminothiazolines that we obtained showed a considerable shift in the absorption bands of the $C=O$ (1600-1610) and $C=N$ (1550 cm^{-1}) groups; this is due to conjugation of these groups in imine structure I. These data confirm the conclusions in [4, 5] regarding the imine structure of 2-acyliminothiazolines and are applicable to the 2-benzamido-5-methylenethiazolines (I) that we obtained. The absorption band of an amide carbonyl group is observed at 1700 cm^{-1}, and absorption of a $C=N$ group is observed at 1618-1627 cm^{-1} in the IR spectra of the hydrochlorides (IIa-f) of the compounds obtained. The changes in the IR spectra of the hydrochlorides can be explained by the fact that salt formation proceeds through formation of a cation at the ring nitrogen.



Three absorption maxima are noted in the UV spectra of the 2-benzamidothiazolines (Table 3); a maximum, characteristic for the thiazoline ring, is observed at 197 nm and below [6]. A bathochromic shift of the maximum by 10 nm and higher with no changes in the positions of the two other maxima (270 and 235 nm) arises during the formation of the hydrochlorides. A similar shift in the maxima in the UV spectra during the formation of hydrochlorides is also observed in the case of thiazolidines with a fixed structure, while the absorption maxima of thiazolines and their hydrochlorides coincide [1]; this confirms the assumption regarding the amine structure of hydrochlorides IIa-f.

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TABLE 1. Physical Constants and Yields of I

Compound	R	R′	mp, °C	mp of the hydrochloride, °C	R_f †	Empirical formula	Found, %			Calc., %			Yield, %
							C	H	S	C	H	S	
Ia	CH_3	CH_3	110	187—188	0,36	$C_{13}H_{14}N_2OS$	63,4	6,1	12,7	63,4	5,7	13,0	75,6
Ib	CH_3	C_2H_5	130—131	188—190	0,38	$C_{14}H_{16}N_2OS$	64,5	6,4	12,7	64,6	6,2	12,3	92,5
Ic	CH_3	C_3H_7	126	218—220	0,34	$C_{15}H_{18}N_2OS$	65,9	6,6	11,2	65,7	6,6	11,7	82,4
Id	C_2H_5	C_2H_5	91—92	114—115	0,32	$C_{15}H_{18}N_2OS$	65,1	6,5	11,8	65,7	6,6	11,7	80,2
Ie	$—(CH_2)_4—$		99—100	154—155	0,30	$C_{15}H_{16}N_2OS$	66,2	6,1	11,4	66,2	5,9	11,8	70,0
If	$—(CH_2)_5—$		134—135	209—210	0,39	$C_{16}H_{18}N_2OS$	67,3	6,3	11,1	67,1	6,3	11,2	88,1

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* The composition of hydrochlorides IVa-f was confirmed by determination of the percentage of nitrogen.

† The adsorbent was Al_2O_3, the eluent was benzene, and the developer was iodine.

TABLE 2. PMR Spectra of I

Compound	Solvent	Chemical shifts of the $>C=C<^{H_1}_{H_2}$ protons, δ, ppm		Δδ, ppm	J, Hz
		H_1	H_2		
Ia	CCl_4	5,16	5,08	0,08	1,7
Ib	CCl_4	5,10	4,90	0,20	2,0
Ic	CCl_4	5,14	5,07	0,07	2,0
Id	CS_2	5,08	4,88	0,20	2,0
Ie	CS_2	5,00	5,00	—	—
If	CS_2	5,00	5,00	—	—

TABLE 3. Data from the IR and UV Spectra of I and II

Compound	IR spectra, ν, cm^{-1}				UV spectra of I					
	bases		hydrochlorides		λ_{max}, nm			lg ε		
	C=O	C=N	C=O	C=N						
Ia	1625	1550	1700	1615	197,5	240	279	2,02	1,65	1,79
Ib	1605	1530	1700	1610	—	240	279	—	1,78	1,91
Ic	1600	1550	1700	1610	—	241	280	—	1,72	1,91
Id	1610	1545	1700	1600	197,5	242	280	2,14	1,87	2,06
Ie	1635	1550	1700	1610	198,0	241	280	2,12	1,79	1,93
If	1630	1550	1700	1605	—	242	280	—	1,71	1,85

EXPERIMENTAL

The IR spectra were recorded with a UR-20 spectrometer. The PMR spectra of CCl_4 and CS_2 solutions were recorded with a ZKR-60 spectrometer with hexamethyldisiloxane (HMDS) as the standard. The UV spectra of alcohol solutions were recorded with a Hitachi EPS-3T spectrophotometer with a deuterium lamp.

2-Benzamido-4,4-dimethyl-5-methylenethiazoline (Ia). A 3.26 g (0.02 mole) sample of benzoyl isothiocyanate was added dropwise with stirring and cooling to 1.66 g (0.02 mole) of 3-amino-3-methyl-1-butyne; the temperature of the mixture was kept below 50° (the reaction was exothermic). The mixture was cooled, and the precipitated Ia was purified by recrystallization from dry petroleum ether to give 3.72 g (76.5%) of a product with mp 110° and R_f 0.36 (activity III Al_2O_3, elution with benzene). Found, %: C 63.4; H 6.1; S 12.7. $C_{13}H_{14}N_2OS$. Calculated, %: C 63.4; H 5.7; S 13.0.

The hydrochloride of IIa was obtained by addition of an ether solution of HCl to an ether solution of Ia. The luminous precipitate was removed by filtration and washed with ether to give a product with mp 187-188°. Found, %: N 10.0. $C_{13}H_{14}N_2OS \cdot HCl$. Calculated, %: N 9.9.

Compounds Ib-f were similarly obtained (Table 1).

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