Hydrolysis of Methyl 1,1-Dioxo-3-thiolanylcarbamate (V). A solution of 19.3 g (0.1 mole) of carbamate V and 6 g (0.11 mole) of KOH in 100 ml of water was refluxed for 20 h, after which it was cooled and filtered. The filtrate was evaporated, and the residue was dissolved in chloroform. Dry HCl was passed into the solution at no higher than 10-15°C until it became acidic. The precipitated hydrochloride of VI was separated to give 14.2 g (83%) of a product with mp 218-219°C.

Hydrolysis of Phenylcarbamates I and Carbonates VII. This reaction was carried out by refluxing 0.02-0.2 M solutions of the compounds in water or a mixture of solvents in the presence of equimolar amounts of bases for 5 h. The solutions were evaporated, and the residues were dissolved in acetone and analyzed by GLC. The results of hydrolysis are presented in Table 1.

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DIHYDRO-1,2,3-TRIALKOXYCARBONYLCYCLOPENTA[b]-1,4-BENZOTHIAZINES

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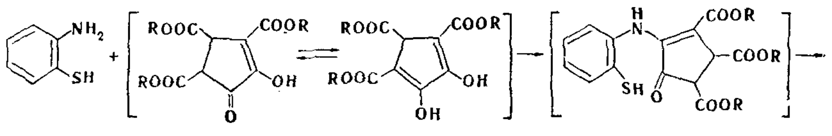
L. S. Degtyarev, and G. F. Dvorko

UDC 547.869

3a,9-Dihydro-1,2,3-trialkoxycarbonylcyclopenta[b]-1,4-benzothiazines, the structures of which were established on the basis of the absorption, fluorescence, PMR, and IR spectra and quantum-chemical calculations, were synthesized by condensation of o-aminothiophenol with 1,2-dihydroxy-3,4,5-trialkoxycarbonyl-2,5-cyclopentadienes.

Little study has been devoted to 1,4-benzothiazines, and they have not yet found any practical application [1]. Several cyclopenta-1,4-benzothiazines, which were obtained by condensation of o-aminothiophenol with 2-chlorocyclopentanone [2], 3-chlorocyclopentane-1,2-dione [3], indanedione [4], and 2-hydroxytrialkoxycarbonylcyclopentadienone [5], are described in the literature. We have found that the condensation of o-aminothiophenol with 1,2-dihydroxy-3,4,5-trialkoxycarbonyl-2,5-cyclopentadienes* leads to 3a,9-dihydro-1,2,3-trialkoxycarbonylcyclopenta[b]-1,4-benzothiazines (V) [7]:



I II III

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*The compounds exist in solution in the form of a tautomeric mixture of the keto enol and the dienediol [6].

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TABLE 1. 3a,9-Dihydro-1,2,3-trialkoxycarbonylcyclopenta[b]-1,4-benzothiazines (V) and 2,3,3a,9-Tetrahydro-3a-hydroxy-1,2,3-trimethoxycarbonylcyclopenta[b]-1,4-benzothiazine (IVa)

Compound	R	mp, °C	ν* NH, cm⁻¹	ν* OH, cm⁻¹	Found, %				Empirical formula	Calculated, %				Yield, %
					C	H	N	S		C	H	N	S	
IVa	CH_3	202—204	3330	3370	54,2	4,4	3,9	8,4	$C_{17}H_{17}NO_7S$	53,8	4,5	3,7	8,4	73
Va	CH_3	180—181	3320	—	56,5	4,2	3,9	8,9	$C_{17}H_{15}NO_6S$	56,5	4,2	3,9	8,9	78
Vb	C_2H_5	138—139	3320	—	59,2	5,2	3,5	8,0	$C_{20}H_{21}NO_6S$†	59,5	5,2	3,5	8,0	80
Vc	$CH(CH_3)_2$	75	—	—	61,6	6,2	3,3	7,2	$C_{23}H_{27}NO_6S$	62,0	6,1	3,1	7,2	21

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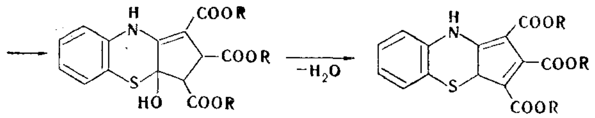
*In KBr pellets.

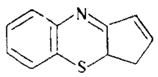
†Found: M 420 (by cryoscopy in benzene). Calculated: M 403.5.



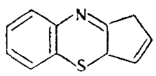
IV V

I—V: a $R=CH_3$; b $R=C_2H_5$; c $R=CH(CH_3)_2$

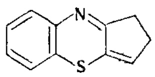
Only one of the eight possible tautomeric forms (V-XII) is realized:



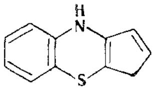
VI



VII



VIII



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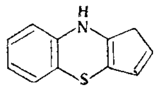
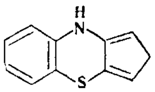


X



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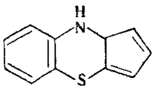
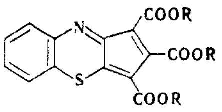


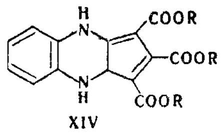
XII

Intermediate IVa, which is a colorless finely crystalline substance that can be converted to Va by heating a solution of it in dimethylformamide (DMF) or acetic acid above 100°C, was isolated from the reaction mixture when the reaction with IIa was carried out in ethanol. The dehydration of IVa to give Va takes place in the cold in pyridine. Heating the starting compounds in acetic acid, DMF, or pyridine and without a solvent leads to the production of only final product V (Table 1).

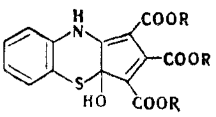
Compounds V are yellow finely crystalline substances that are only slightly soluble in ether, hexane, and CCl_4 but soluble in acetone, alcohols, chloroform, and acetic acid. Compound Vc is quite soluble in most organic solvents. Compound Vb is oxidized to benzothiazine XIII, the electronic spectrum of which coincides with the spectra of genuine samples [5], when oxygen is blown through a solution in CCl_4 and when it is irradiated with a quartz lamp.



XIII



XIV



XV

TABLE 2. PMR Spectra of IVa and V

Compound	Solvent	Position of the protons	δ, ppm	No. of protons, multiplicity (J, Hz)
IVa	$CDCl_3$	1,2,3-$(COOCH_3)_3$	3,71; 3,74; 3,81	3, s; 3, s 3, s
		2-H and 3-H	3,58; 4,10	1, d (8,4); 1, d (8,4)
		3a-OH	4,10	1, s
		5,6,7,8-H_4	6,65—7,33	4, s
		NH	9,23	1, s
Va	$CHCl_3$	1,2,3-$(COOCH_3)_3$	3,81; 3,85; 3,90	3,s ; 3, s ; 3,s
		3a-H	4,74	1, s
		NH	9,44	4, m
Vb	$CHCl_3$	CH_3	1,29; 1,31; 1,34	3, t (7,0); 3, t (7,0); 3, t (7,0)
		OCH_2	4,23; 4,28; 4,33	2, q (7,0); 2, q (7,0); 2, q (7,0)
		3a-H	4,68	1, s
		NH	9,50	1, s
Vb	CCl_4	CH_3	1,08—1,44	18, m
		OCH and 3a-H	4,67—5,39	4, m
		5,6,7,8-H_4	6,96	4, m
		NH	9,50	1, s

An absorption band of an NH group with an intramolecular hydrogen bond appears in the IR spectra of KBr pellets of V. The IR spectrum of IVa also contains the band of an OH group at 3370 cm^{-1} (Table 1). The absorption at 2500 cm^{-1} that is characteristic for the SH group is absent. This indicates that the intermediate has structure IV rather than III. The PMR spectra of V in chloroform (Table 2) contain signals of the proton of the NH group (9.5 ppm) and the proton of the cyclopentane ring (4.7 ppm). The assignment of the signal for the proton of the NH group was made on the basis of the fact that it is found at 8.7 ppm in the case of dihydrotrialkoxycarbonylcyclopentaquinoxalines XIV [8].

These data constitute evidence that tautomers VI-VIII are not formed in our case.

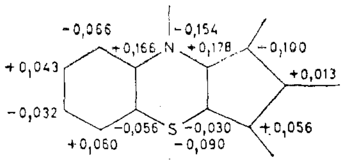
The existence of fluorescence in V indicates the absence of tautomers IX and X, since in these tautomers the central ring, which contains eight π electrons, would be noncoplanar, and they would not be able to fluoresce [9].

The final selection from the three remaining structures was made on the basis of quantum-chemical calculations of the electronic structure of XI (the self-consistent process diverges for structures V and XII). According to these calculations, of the three carbon atoms of the cyclopentane ring, viz., 2, 3a, and 9a, the electron density is maximal on the 3a atom, to which a hydrogen atom is also evidently attached (Fig. 1).

Structure V is confirmed by the data from electronic spectroscopy. The compounds obtained display spectra with a well-resolved vibrational structure at 340-450 nm (Fig. 2). A slight (10 nm) bathochromic shift is observed on passing from dihydrocyclopentaquinoxalines XIV to dihydrocyclopentabenzothiazines V, i.e., when the nitrogen atom is replaced by a sulfur atom; this can be explained by the fact that the sulfur atom yields its electrons to the overall system less readily [5].

Like the spectra of quinoxalines XIV, the spectra of V are similar to the electronic spectra of 3a,9-dihydro-3a-hydroxy-1,2,3-trialkoxycarbonylcyclopenta[b]-1,4-benzothiazines (XV) [5] both with respect to the position of the maxima and their intensities. In contrast to quinoxalines XIV, the proton of the NH group is not split out by the action of aqueous alcoholic alkali on V; instead, one observes the formation of anion XVI, in which the charge is concentrated on the oxygen atoms that is evidently in the α position relative to the nitrogen atom rather than to the sulfur atom. This conclusion was drawn on the basis of the fact that the formation of anion XVIII from XV is also accompanied by a hypsochromic shift; however the spectra of XVI and XVIII are not identical.

Orange-red solutions are formed when V and IVa are dissolved in CF_3COOH or mineral acids (Fig. 2), this is associated with protonation



XI

Fig. 1

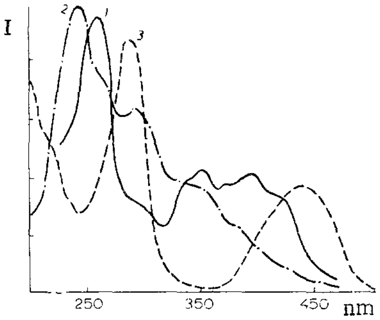
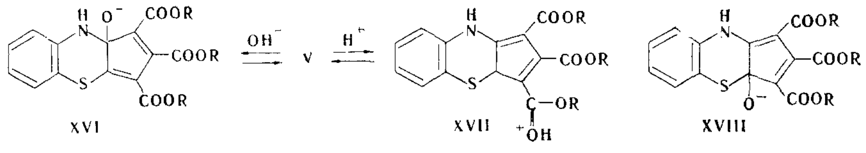


Fig. 2

Fig. 1. Molecular diagram of XI.
Fig. 2. Electronic spectra of 3a,9-dihydro-1,2,3-triethoxycarbonylcyclopenta[b]-1,4-benzothiazine (Vb) and its anion (XVIb) and cation (XVIIb): 1) Vb; 2) XVIb; 3) XVIIb (I is the relative intensity).



XVI XVII XVIII

of the carbonyl group and the formation of cation XVII [8]. The absorption spectrum of IVa differs considerably from the spectra of V. The decrease in the number of bands and the strong hypsochromic shift in the spectrum of IVa indicate shortening of the π-electron conjugation chain.

EXPERIMENTAL

The electronic spectra were recorded with a Unicam SP-8000 spectrophotometer; all of the investigated solutions obeyed the Bouguer–Lambert–Beer law at concentrations of 10^{-5} to 10^{-4} mole/liter. The IR spectra were recorded with a UR-20 spectrometer. The PMR spectra were recorded with a Tesla BS-477 spectrometer (60 MHz) with hexamethyldisiloxane as the internal standard. A solution of anion XVIb was obtained by dissolving Vb in a 0.01 mole/liter alcohol solution of KOH, and the XVIIb cation was obtained by dissolving Vb in 70% H_2SO_4. The molecular diagram of V was calculated by the CNDO/2 method by means of the QCPE-141 program with the parameters in [10] and with a BESM-6 computer with a Duban monitoring system. The bond lengths and angles were taken from [11].

2,3,3a,9-Tetrahydro-3a-hydroxy-1,2,3-trimethoxycarbonylcyclopenta[b]-1,4-benzothiazine (IVa). A solution of 0.50 g (4 mmole) of o-aminothiophenol in 10 ml of ethanol was added to 1.09 g (4 mmole) of IIa dissolved by heating in 20 ml of ethanol, and the mixture was heated to the boiling point. After a certain length of time, a white precipitate formed. The reaction mixture was cooled, and the reaction product was removed by filtration and purified by reprecipitation from solution in DMF by the addition of water.

3a,9-Dihydro-1,2,3-trimethoxycarbonylcyclopenta[b]-1,4-benzothiazine (Va). A solution of 1.14 g (3 mmole) of IVa in 30 ml of acetic acid was refluxed for 30 min. The solution rapidly turned yellow. The solvent was evaporated partially in vacuo, and the residue was diluted with water. The precipitated Va was removed by filtration and purified by crystallization from acetone.

3a,9-Dihydro-1,2,3-triethoxycarbonylcyclopenta[b]-1,4-benzothiazine (Vb). A solution of 0.63 g (5 mmole) of o-aminothiophenol in 10 ml of ethanol was added to a solution of 1.57 g (5 mmole) of IIb in 20 ml of ethanol, and the mixture was heated to 120°C and maintained at this temperature without a reflux condenser for 1 h (the ethanol evaporated, and the reaction took place without a solvent). The reaction mixture was cooled, triturated and washed with small portions of ether, and purified by crystallization from acetone.

3a,9-Dihydro-1,2,3-triisopropoxycarbonylcyclopenta[b]-1,4-benzothiazine (Vc). This compound was similarly obtained and was purified by reprecipitation from a solution in ethanol by the addition of a dilute solution of sodium carbonate.

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AZIRIDINYL KETONES AND THEIR HETEROANALOGS.

5.* SYNTHESIS AND STRUCTURES OF 2-ARYL-3-AROYLAZIRIDINES

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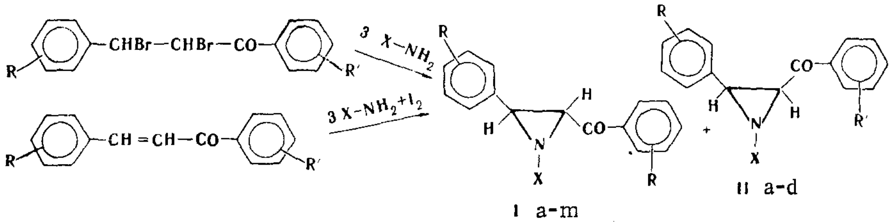
and V. F. Lavrushin

UDC 547.717.07:541.621'571.9

A number of trans- and cis-isomeric 1-R-2-aryl-3-aroylaziridines were synthesized, and their IR spectra were studied. Intramolecular hydrogen bonding is realized in the trans isomers when R = H, and they exist in the only possible conformation (intermediate between a gauche and a cisoid conformation). cis-Isomers II (R = alkyl) exist in solutions in the form of two conformers, viz., gauche and cisoid conformers, and the gauche conformer is thermodynamically preferable.

The chemistry of aziridinyl ketones has been the subject of many studies (for example, see review [2]). However, some problems relative primarily to NH compounds remain unsolved.

The present communication is devoted to a study of 2-aryl-3-aroyl-aziridines of the trans (I) and cis (II) series. Their synthesis was accomplished by the Gabriel–Cromwell method (by reaction of α, β-dibromochalcones with amines [3]) and by the Soutwick method (by reaction of chalcones with iodine and an amine [4]):



I a-m

II a-d

(R, R', and X are indicated in Table 1)

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*See [1] for Communication 4.

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