mixed with 1.2 g (0.03 mole) granulated sodium hydroxide for 40-50 min until a voluminous precipitate of the salt IIa formed, after which mixing was continued for another 10-15 min. The reaction mixture was removed by decanting from the alkali granules, the salt was filtered off and dried under vacuum (1-2 mm Hg, 100°C) over 3 Å molecular sieves to constant weight. Yield 0.54 g (50%), t. decomp. 250-252°C. UV spectrum, λmax (log ε): 265 nm (4.22). IR spectrum: 1665 (C), 1620 (CN), 1530 cm⁻¹ (CN). PMR spectrum, δ: 7.09-7.57 (m, Ph), 3.77 ppm (s, 5H). Found: C 51.0; H 3.4; N 13.0; S 14.8%. C₉H₇N₂NaOS. Calculated: C 50.5; H 3.3; N 13.1; S 15.0%.

Potassium Salt of 2-Phenylimino-4-thiazolidinone (Ib). Produced analogously to compound Ia. Yield 0.67 g (60%), t. decompt. 250-253°C. UV spectrum, λmax (log ε): 265 nm (4.22). IR spectrum: 1635 (CO, CN), 1545 (CN), 1520 cm⁻¹ (CN). Found: C 47.2; H 3.5; N 11.8; S 13.6%. C₉H₇KN₂OS. Calculated: C 46.9; H 3.1; N 12.2; S 13.9%.

Cesium Salt of 2-Phenylimino-4-thiazolidinone (Ic). Produced analogously to compound Ia. Yield 0.67 g (40%), t. decompt. 220-230°C. UV spectrum, λmax (log ε): 265 nm (4.20). IR spectrum: 1640 (CO), 1610 (CN), 1550 (CN), 1540 cm⁻¹ (CN). Found: C 33.1; H 2.6; N 8.6; S 9.9%. C₉H₇C₆N₂SO. Calculated: C 33.4; H 2.2; N 8.6; S 9.9%.

SYNTHESIS AND STRUCTURE OF 1,1-DIOXIDES OF 3-ALLYL(STYRYL)-4H-1,2,4-BENZOTHIAZIDIAZINE

V. S. Fedenko, Z. F. Solomko, and V. I. Avramenko

The reaction of o-aminobenzenesulfonamides with acids of crotonic and cinnamic acids in dioxane yielded the corresponding anilides, which were cyclized to derivatives of 1,2,4-benzothiadiazine 1,1-dioxide. The structure of the end products is discussed in connection with the possibility of tautomeric equilibrium of the 2H- and 4H-forms on the basis of the spectral data.

Derivatives of benzothiadiazine, which contain an alkenyl substituent in the 3-position of the heterocyclic ring, possess pronounced hypotensive activity [1, 2], comparable with the action of diazoxide in clinical use [3]. According to the spectral data [4, 5], and quantum chemical calculations [6], 1,1-dioxides of 1,2,4-benzothiadiazine exist primarily in the 4H-form. In view of this it is of interest to evaluate the influence of a substituent with a multiple bond on the state of the tautomeric equilibrium.

For this purpose we synthesized some 1,1-dioxides of 3-allyl(styryl)-4H-1,2,4-benzothia-
diazine (IIa-d) by heterocyclization of o-sulfamoylanilides of crotonic and cinnamic acids (IIa-c) under the action of alkali (Table 1). The anilides II in turn were produced from o-aminobenzenesulfonamides (Ia-d) and chlorides of crotonic and cinnamic acids in dioxane. Since the N-methylcrotonanilide IIc is hydrolyzed in alkaline medium to the initial o-N-methylamino-benzenesulfamide (Id), thermal cyclization of the anilide IIc was used to synthesize the dioxide IIIc.

The structure of compounds IIa-d was confirmed by spectral data. It should be noted that the frequencies of the stretching vibrations of the C-C and C-O bonds in the IR spectrum of compound IIc are shifted in the low-frequency direction in comparison with croton-
The observed UV absorption of compounds IIa-d (Fig. 1) is the result of superposition of two conjugated chromophores $\rightarrow$N-C$_6$H$_5$SO$_2$NH$_2$ and R-CH=CH-C=O. The latter chromophore (for example, in crotonic acid [7]) has a band at 205 nm; therefore its influence on the general nature of the spectrum will be negligible. As a result of this, three bands are observed in the electronic spectra of the anilides Ia and b, just as for orthoanilamide [8]. The introduction of a chlorine atom into the ring causes a bathochromic shift of the indicated bands, which agrees with the influence of electron acceptor substituents on the absorption of the aromatic chromophore [9]. The sharp difference of the spectrum of the N-methylcrotonanilide IIId is evidently due to a disruption of the coplanarity of the $\pi$-electrons of the phenyl ring and the $p$-electrons of the unshared pair of the nitrogen atom, which is associated with the presence of a voluminous ortho-sulfamoyl group. Therefore, the spectrum of compound IIId becomes close to the absorption of benzenesulfamide [10]: $\lambda_{\text{max}}$ (log $\varepsilon$): 218 (3.99), 265 nm (2.87). The strong hyperchromic effect of the long-wave band in the electronic spectrum of the anilide IIc is evidence of the realization of an extended chromophore system.

In the PMR spectrum of the crotonanilide IIa (acetone-D$_6$), the protons of the CH$_3$ and CH groups form an ABX$_3$-spin system. The signal of the methyl protons is represented in the form of a quartet at 1.83 ppm ($J_1 = 3.5$ and $J_2 = 1.5$ Hz). The signal of the methine proton in the allyl position appears in the form of two quartets with a center at 5.93 ppm. This assignment is supported [11] by the value of the allyl constant $J_2$ (1.5 Hz), while the value of the constant $J_3$ (16 Hz) permits a transconfiguration to be ascribed to the anilide IIa, by analogy with crotonic acid [12]. The signal of the other methine proton forms a complex multiplet with sulfamide and aromatic protons in the region of 6.57-8.70 ppm, while the broadened signal (9.53 ppm) indicates the presence of an amide NH group in the structure.

The conversion of the anilides IIa-d to the dioxides IIIa-d is indicated by the disappearance of the "amide I" band in the IR spectra of the latter, the appearance of absorption of the C=O bond [1, 13], at 1615-1618 cm$^{-1}$, a low-frequency shift (40-45 cm$^{-1}$) of the asymmetrical stretching vibrations of the SO$_2$ group, and changes in the region of the stretching vibrations NH. An unsaturated substituent in the 3-position does not change the nature of the absorption in the region of 1500-1620 cm$^{-1}$, which, just as for other 1,2,4-benzothiadiazines, is characterized by three strong bands [14]. The absorption in the region of 3150-3265 cm$^{-1}$ is represented by a complex set of bands with different relative intensities. Earlier [1] the absorption at 3075-3290 cm$^{-1}$ of 3R-1,2,4-benzothiadiazines was assigned to the stretching vibrations of N-H. For the 1,1-dioxide of 3-methylbenzothiazolide, the interpretation of the short-wave band at 3260 cm$^{-1}$ is confirmed by the method of deuteration [15]. Our investigation of a deuteroanalog of the dioxide IIIb permitted an experimental confirmation of the presence of three bands $\nu$N-H (Table 1): the calculated values of $\nu$N-D/ $\nu$N-H lie in the interval 1.35-1.38. The stretching vibrations of =C-H in the region of 3065-3095 cm$^{-1}$ differ appreciably from the absorption of C-H of the methyl group (2848-2978 cm$^{-1}$). We should mention that the asymmetrical vibration $\nu$C-H is split into two bands with lower intensity as a result of the resonance effect [16] due to the presence of a neighboring double bond. The broad, low-intensity band in the spectra of the dioxides IIIa-c in the region of 2780-2795 cm$^{-1}$ is characteristic of the strongly associated N-H bond [17].

Thus, the electronic spectra of compounds IIIa and the model 1,1-dioxide of 3-methyl-1,2,4-benzothiadiazine, which, according to the data of [4], is represented in alcohol solution by a 4H-form, differ substantially (Fig. 2), it might have been assumed that when the methyl group is replaced by an allyl group, the equilibrium will be shifted in the direction of the 2H-form.

However, a comparison with the 4-methyl derivative IIIId, where the C=N bond is rigidly fixed in the 2,3-position, supports a 4H form. The change in the nature of the UV absorption