C=N and C—O—C (in the oxazoles) or C—O—N (in the isoxazoles) group moments. In oxazole, the moments of these groups have opposite directions and in isoxazole they are in the same direction. If a moment of 2.47 D is assumed for the C=N bond [2] and moments of 0.8, 0.45, 0.5, and 0.4 D, respectively, for the C—O, C—N, N—O, and C—H bonds, then for oxazole and isoxazole by vector addition we obtain, respectively, 1.35 and 3.90 as compared with the observed values of 1.4 and 2.8 D.

The moment of 2,5-diphenyl-1,3-oxazole was calculated vectorially from the moments of the $\mu_{\overrightarrow{C=N}}$, $\mu_{\overrightarrow{C-O}}$, $\mu_{\overleftarrow{C-H}}$, $\mu_{C_{ar-2} \overleftarrow{-} C_{het}}$ and $\mu_{C_{ar-5} \overrightarrow{-} C_{het}}$, bonds equal, respectively, to 2.47, 0.8, 0.4, 0.4, and 0.4 D; the angles between all the bonds in the heterocycle were taken as the same and equal to the angle in a regular pentagon. The calculated moment proved to be 1.29 D (as compared with the observed 1.55 D) with an angle of inclination of the vector of this moment to the nominal axis of symmetry of the molecule passing through the oxygen atom and the center of the C_4—N bond of 32°. The calculated values of the moments of the derivatives with para substituents in the phenyl group are given in Table 1. In the calculation, values of the moments of substituted benzenes C_6H_5X with $X = NO_2$, C_6H_5, Br, and OCH_3 equal, respectively, to 4.00, 0.4, 1.52, and 1.31 D were used and the angle of inclination at $X = OCH_3$ was taken as 67°. As can be seen from Fig. 2, the values of $\Delta\mu = \mu_{obs} - \mu_{calc}$ correlate satisfactorily, except for X = Br, with $\Delta E_{1/2}$ — the increase in the polarographic reduction potential of a nitro or carbonyl group under the influence of X [4, 5], which shows the existence of appreciable conjugation between the electrons of the substituent X through the phenyl group with the π-electrons of the heterocycle.

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THIONYLAMIDES AND THIONYLAMIDINES OF CARBOXYLIC ACID

L. I. Samarai, V. P. Belaya, and G. I. Derkach

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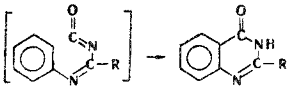
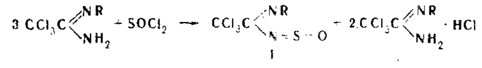
Amidines of carboxylic acids react with thionyl chloride to form thionylamidines which are converted spontaneously into 2H-1,2,4-benzothiadiazine 1-oxides. Carbimidic esters react with thionyl chloride to give thionylamides as final products.

In preceding communications [1, 2] we have shown that isocyanates of carbimidic acids are converted into 4-quinazolones at the moment of their formation.

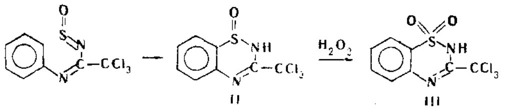


It was of interest to study the properties of the thionylamidines, the sulfur analogs of the isocyanates of carbimidic acids. The thionylamidines were obtained with quantitative yields by the reaction of amidines of carboxylic acid with thionyl chloride in carbon tetrachloride at 50° C.



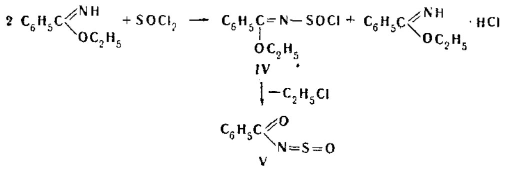
R = C_6H_5, $C_6H_4CH_3$-*p*

Compounds I consist of orange-colored crystalline substances with low melting points, readily soluble in organic solvents and readily hydrolyzed by atmospheric moisture to the initial amidines. The IR absorption spectra of compounds I have a strong band in the 1260 cm^{-1} region which is ascribed to the —N=S=O group [3, 4]. On being stored in a closed vessel at room temperature, compound I (R = C_6H_5) is converted spontaneously after 2–4 days into 2H-1,2,4-benzothiadiazine-1-oxide (cf. [5, 6]).



The action of 30% hydrogen peroxide in acetic acid on compound II gives 2H-1, 2, 4-benzothiadiazine 1, 1-dioxide.

With thionyl chloride in an inert solvent, ethyl benzimidate gives the acid chloride IV, which is split into ethyl chloride and N-thionylbenzamide on being heated to 120–130° C.



Compound V is an orange liquid. It is readily miscible with organic solvents and is instantaneously hydrolyzed to benzamide by the action of atmospheric moisture. The IR absorption spectrum of V has a strong band in the 1250 cm^{-1} region which is characteristic for the —N=S=O group.

EXPERIMENTAL

Thionylamidines (I). A solution of 0.03 mole of thionyl chloride in 20 ml of carbon tetrachloride was added to a suspension of 0.09 mole of an amidine in 100 ml of anhydrous carbon tetrachloride cooled with ice water. The reaction mixture, which was colored orange, was stirred at room temperature for another 0.25–0.5 hr. Then the temperature was raised to 50° C and stirring was continued for another 2–3 hr. The precipitate of amidine hydrochloride was separated off under conditions excluding atmospheric moisture and was washed several times with small portions of carbon tetrachloride. The filtrate was evaporated in vacuum. The residue consisted of the crystalline thionylamidine in a yield of about 95%. Compounds I can be recrystallized from a small amount of petroleum ether. Compound I (R = C_6H_5) forms light orange needles, mp 40–42° C (in a sealed capillary). IR spectrum, cm^{-1}: 1260 (N=S=O). Compound I (R = = $C_6H_4CH_3$-p) forms bright orange needles, mp 70–72° C (in a sealed capillary). IR spectrum, cm^{-1}: 1260 (N=S=O).

Since the thionylamidines are readily hydrolyzed by atmospheric moisture, they were identified in the form of the corresponding amidines after treatment with water.

2H-1, 2, 4-Benzothiadiazine-1-oxide (II). Compound I (R = C_6H_5) (0.002 mole) was left to stand in a sealed vessel for 2–4 days. The color of the crystals changed from yellow-orange to yellow-green and the shape of the crystals from needles to a microcrystalline powder. The reaction product was washed with small portions of ether and dried. The yield of II was 67%. The substance is sparingly soluble in the usual organic solvents and crystallizes from ethyl acetate in the form of light yellow prisms, mp 183° C (decomp.). In the IR spectrum of II, the band in the 1250 cm^{-1} region characteristic for the N=S=O group is absent. Found, %: S 11.15; N 9.74. Calculated for $C_8H_5Cl_3N_2O_2S$, %: S 11.31, N 9.88.

2H-1, 2, 4-Benzothiadiazine-1, 1-dioxide (III). A suspension of 0.001 mole of II in 10 ml of glacial acetic acid was treated with 2 ml of perhydrol and heated at 60° C for 10–15 hr. The precipitate of III was filtered off, washed with water, and dried. The yield of III was 90%. Light yellow needles (from acetone), mp 257° C (decomp.). Found, %: S 10.78; mol. wt. (Rast) 302. Calculated for $C_8H_5Cl_3N_2O_2S$, %: S 10.70; mol. wt. 299.58.

N-Thionylbenzamide (V). In drops, a solution of 0.2 mole of ethyl benzimidate in 40 ml of carbon tetrachloride was added to a solution of 0.1 mole of thionyl chloride in 50 ml of anhydrous carbon tetrachloride cooled with ice water. The reaction mixture was stirred at 20° C for 1 hr. The precipitate of the imidate hydrochloride was filtered off and washed with carbon tetrachloride (3 × 15 ml), and the filtrate was evaporated in vacuum. Compound IV, in the form of an orange liquid, was heated in the oil bath to 120–140° C. Decomposition was accompanied by the evolution of gases and was complete after 1–1 1/2 hr at this temperature. The resulting compound V, a yellow-orange liquid, was distilled in vacuum, bp 77–79° C (0.3 mm), n_D^{20} 1.5735, d_4^{20} 1.2298. Yield 33%.

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Institute of Organic Chemistry,
AS UkrSSR, Kiev