after 10-15 min. After 24 h, the mixture was diluted with water, acidified with HCl, and filtered. The products were crystallized from acetic acid or dioxane.

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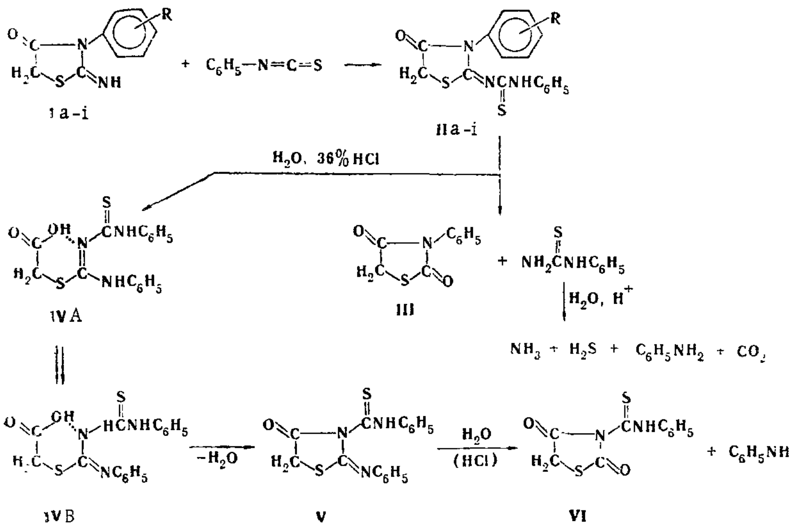
REACTION OF 2-IMINO-3-ARYL-4-OXOTHIAZOLIDINES WITH PHENYL ISOTHIOCYANATE

Yu. V. Svetkin, S. A. Vasil'eva, and L. D. Tokareva

UDC 547.789.1.5

2-Phenylthiocarbamoylimino-3-aryl-4-oxothiazolidines, which are hydrolyzed at the C = N and $N_3 = C_4$ bonds of the thiazolidine ring to give 3-arylthiazolidine-2,4-diones, N-phenylthiocarbamoylarylpseudothiohydantoic acids, and 3-phenylthiocarbamoylthiazolidine-2,4-dione, were synthesized by reaction of 2-imino-3-aryl-4-oxothiazolidines with phenyl isothiocyanate.

In order to obtain compounds with possible physiological activity we investigated the addition of phenyl isothiocyanate to the imino group of 2-imino-3-aryl-4-oxothiazolidines Ia-i to give 2-phenylthiocarbamoylimino-3-aryl-4-oxothiazolidines IIa-i in high yields.



Bashkir State University, Ufa. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 903-905, July, 1976. Original article submitted August 20, 1975.

TABLE 1. 2-Phenylthiocarbamoylimino-3-aryl-4-oxothiazolidines IIa-i

Compound	R	mp, °C*	Empirical formula	Found, %			Calc., %			λ_{max}, nm (lg ε)	Yield, %
				C	H	N	C	H	N		
IIa†	H	191—192	$C_{16}H_{13}N_3OS_2$	58,4	4,1	12,2	58,7	4,0	12,8	245 (4,15) 405 (4,02)	85
IIb	p-CH_3	189—190	$C_{17}H_{15}N_3OS_2$	59,5	4.5	12.4	59,8	4,4	12,3	278 (4,16) 413 (4,07)	94
IIc	p-OCH_3	186—187	$C_{17}H_{15}N_3O_2S_2$	57.9	4,7	11,3	57,1	4,2	11.6	264 (4,23) 420 (4,02)	89
IId	p-OC_2H_5	193—194	$C_{18}H_{17}N_3O_2S_2$	58,2	4,1	11,6	58,2	4,2	11,3	261 (4,28) 414 (4,04)	80
IIe	m-Cl	179—180	$C_{16}H_{12}N_3OS_2Cl$	53,0	3,2	12,2	53,1	3,3	11.6	336 (3,96)	85
IIf	p-Br	190—191	$C_{16}H_{12}N_3OS_2Br$	47,5	2,8	10,1	47.3	3.0	10.3	412 (3.94)	90
IIg	p-NO_2	193—194	$C_{16}H_{12}N_4O_3S_2$	51,3	3,1	14,5	51,6	3,2	15,0	270 (4,20) 370 (4,10)	70
IIh	p-C_7H_{15}	173—174	$C_{23}H_{27}N_3OS_2$	64,3	6,2	9,5	64,5	6,4	9,9	266 (4,21) 414 (3,98)	75
IIi	m-NO_2	184—185	$C_{16}H_{12}N_4O_3S_2$	51,7	3.4	14,4	51,6	3.2	15.0	300 (4,25) 403 (4,08)	70

* From dioxane.

†Found: M 324 (mass spectrometrically). Calculated: M 327.

Two intense thioamide bands at 1120 and 1150 cm^{-1} are observed in the IR spectra of IIa-i, whereas the absorption of a free NH group at 3300 cm^{-1} [1] is absent. Like the spectra of the starting 4-thiazolidinones (Ia-i), the IR spectra of products IIa-i contain an intense absorption band of the stretching vibrations of the CH_2S grouping [2] at 1245 cm^{-1}; this excludes reaction of phenyl isothiocyanate at the methylene group.

The electronic spectra of IIa-i consist of bands at 245-300 nm peculiar to 4-thiazolidinones [2] and a second band at 400-418 nm related to the absorption of the thiocarbonyl group [1].

Compound IIa is hydrolyzed at the C = N bond to give 3-phenylthiazolidine-2,4-dione III and phenylthiourea, which subsequently decomposes to ammonia, hydrogen sulfide, aniline, and carbon dioxide. The thiazolidine ring is cleaved at the $N_3 = C_4$ bond on prolonged heating in hydrochloric acid to give N-phenylthiocarbamoylphenylpseudothiohydantoic acid IV. Acid IV, which can exist in two tautomeric forms ($A \rightleftarrows B$), is cyclized to 2-phenylimino-3-phenylthiocarbamoyl-4-oxothiazolidine V, which splits out aniline and is converted to 3-phenylthiocarbamoylthiazolidine-2,4-dione (VI). Intense bands are present in the IR spectrum of acid IV at 1120 (thioamide), 1680 (C = O group of an acid with an intramolecular hydrogen bond), and 3200 cm^{-1} (stretching vibrations of a bonded OH group [1]). The 3-phenylthiazolidine-2,4-dione (III) structure was confirmed by the IR spectra and by alternative synthesis [3]. The IR spectra of 3-phenylthiazolidine-2,4-dione III and 3-phenylthiocarbamoylthiazolidine-2,4-dione VI are similar, and this is an indirect indication of identical ring structures. They contain two intense absorption bands at 1670 and 1720 cm^{-1} due to the stretching vibrations of two C = O groups. In addition, a band at 1120 cm^{-1}, which is characteristic for the absorption of the NHCS group [1], appears in the IR spectrum of VI.

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a UR-10 spectrometer. The electronic spectra of dioxane solutions of the compounds were measured with a Specord-UV-vis spectrophotometer. The molecular weights were measured with an MKh-1303 mass spectrometer at an inlet system and ion source temperature of 250°, an ionizing voltage of 50 V, an emission current of 15 mA, and an accelerating voltage of 2 kV. 2-Imino-3-aryl-4-oxothiazolidines Ia-i were obtained by reaction of arylthioureas with acetochloroacetic anhydride [4].

2-Phenylthiocarbamoylimino-3-phenyl-4-oxothiazolidine (IIa). A 0.6-g (5 mmole) sample of phenyl isothiocyanate was added with stirring to 1 g (5 mmole) of Ia in 40 ml of alcohol. After 24 h, the precipitate was removed by filtration and washed with water to give 1.36 g (85%) of IIa. The remaining II (Table 1) were obtained under similar conditions.

Acid Hydrolysis of IIa. Concentrated HCl (10 ml) was added to 1 g of IIa in 30 ml of dioxane, and the mixture was refluxed for 1 h. It was then cooled and treated with 100 ml of water, and the precipitate was removed by filtration and refluxed in water. The solid material that did not dissolve on refluxing in water was found to be N-phenylthiocarbamoylphenylpseudothiohydantoic acid IV [0.1 g (10%)] with mp 164-165°. Found: C 55.9; H 4.5; N 12.3; S 18.4%; M 338 (mass spectrometrically). $C_{16}H_{15}N_3O_2S_2$. Calculated: C 55.6; H 4.3; N 12.2; S 18.5%; M 345.

Cooling of the aqueous filtrate yielded 0.3 g (30%) of 3-phenylthiocarbamoylthiazolidine-2,4-dione VI with mp 155-156°. Found: C 47.8; H 3.2; N 10.8%; M 229 (in mass-spectrum). $C_{10}H_{10}N_2O_2S_2$. Calculated: C 47.6; H 3.2; N 11.1%; M 232. Evaporation of the hydrochloric acid filtrate gave 0.38 g (38%) of 3-phenylthiazolidine-2,4-dione III with mp 142-143° (no melting-point depression was observed for a mixture of this product with the product obtained by the method in [3]). The hydrochloric acid filtrate was neutralized with 10% Na_2CO_3 solution, saturated with alkali, and extracted with ether. The ether extract was treated with a mixture of acetic acid and acetic anhydride and the mixture was worked up to give acetanilide, with mp 114° (from water), which was identified by a mixed-melting point determination.

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HAMMETT CONSTANTS OF THE PYRROLINE-2,5-DIONE RING

V. D. Romanenko, N. N. Kalibabchuk,
A. A. Rositskii, V. G. Zalesskaya, V. E. Didkovskii,
and S. V. Iksanova

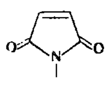
UDC 547.745:543.87

The electronic effect of the pyrroline-2,5-dione ring on the benzene ring in the case of N-aryl compounds is close to the effect exerted by halogens. The overall electron-acceptor effect depends markedly on the nature of the solvent. The electron-donor effect of conjugation is small.

In the present paper we have made a quantitative evaluation of the electronic nature of the pyrroline-2,5-dione (maleinimide) and pyrrolidine-2,5-dione rings within the framework of the Hammett–Taft method.

In conformity with this, we determined the σ constants of pyrroline-2,5-dion-1-yl (I), pyrrolidine-2,5-dion-1-yl (II), and 3-chloropyrrolidine-2,5-dion-1-yl (III) substituents for the para (σ_p) and meta (σ_m) positions with respect to the ionization of p- and m-substituted benzoic acids and, on the basis of the results, estimated, from the Taft equations, the independent contributions and the magnitudes of the substituent constants of the inductive (σ_i) and conjugation (σ_c) effects. The σ_i and σ_c constants found were compared with the corresponding constants calculated on the basis of the F^{19} NMR chemical shifts in the spectra of p- and m-substituted fluorobenzenes.

The information obtained may be of interest in connection with the fact that in recent years maleinimides have received widespread recognition as subjects for the investigation of the chemistry of heterocyclic chain polymers [1].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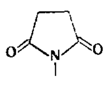
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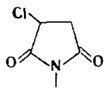

III

The σ constants of substituents I-III in the equation

All-Union Scientific-Research and Design Institute of the Chemical Industry, Kiev. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 906-910, July, 1976. Original article submitted September 1, 1975.