

Thiophene derivatives. III.

Preparation and properties of some 3,5-disubstituted rhodanines

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The synthesis of nine 3,5-disubstituted rhodanines by condensation of 5-(4-nitrophenyl)-2-thiophenecarbaldehyde with 3-substituted aryl-, alkyl-, and aralkylrhodanines is described and the infrared and ultraviolet spectra of these compounds are interpreted.

More than twenty years ago some authors [1–3] prepared series of 5-(5-substituted thenylidene)rhodanines by condensation of the appropriate 5-substituted 2-thiophenecarbaldehydes with rhodanine. 3,5-Disubstituted rhodanines were prepared by similar reaction from 3-substituted rhodanines [4]. The prepared rhodanines showed in most cases fungicidal effects on molds and on fungi appearing on cotton. The most efficient from these compounds appeared to be 5-(2-thenylidene)rhodanine already in 1% concentration.

With regard to the above said, 3-substituted 5-(5-*p*-nitrophenyl-2-thenylidene)rhodanines were synthesized and their i.r. and u.v. spectra interpreted. The possibility of the use of these substances in biological tests as efficient producers of isothiocyanates was considered.

In our work, the above-mentioned compounds were prepared by the condensation method according to *Brown* [4] in the presence of sodium acetate as basic catalyst. The final products were in almost each case isolated by washing the crude product with water, ether, and recrystallization from hot ethanol. All the obtained 3,5-disubstituted rhodanines were orange-red crystalline compounds melting at high temperatures.

Infrared spectra of these compounds showed strong absorption in the range of 1705–1719 cm⁻¹ (Table 2) which could be assigned to the stretching vibration of the carbonyl group. The effect of the substituents in the position 3 of the rhodanine skeleton on the $\tilde{\nu}(\text{C}=\text{O})$ band position was followed. Electron-releasing substituents shifted the stretching vibration of the C=O group to lower wavenumbers (with 3-(4-methoxyphenyl)-5-(5-*p*-nitrophenyl-2-thenylidene)rhodanine $\tilde{\nu}(\text{C}=\text{O})$ was 1705 cm⁻¹), while the electron-accepting substituents did the reverse (with 3-(4-carbethoxyphenyl)-5-(5-*p*-nitrophenyl-2-thenylidene)rhodanine $\tilde{\nu}(\text{C}=\text{O})$ was 1719 cm⁻¹). Vibrations of multiple bonds of the aromatic system were in the range of 1490–1502 and 1590–1600 cm⁻¹; the absorption band at ~1600 cm⁻¹ being more intensive. Very strong absorption bands at 1350–1354 and 1515–1529 cm⁻¹ belonging to *sym* and *as* vibrations of NO₂ group were observed with all derivatives.

All the synthesized derivatives showed two absorption maxima in the u.v. region at 322–329 nm and at 250 nm (belonging to the absorption of the modified benzene ring) and in the visible region at 424–438 nm. An inflexion appeared at about 460 nm

Table 1

Characterization of 3-R-5-(5-*p*-nitrophenyl-2-thenylidene)rhodanine

Compound	R	Formula	<i>M</i>	Calculated/found		Yield [%]	M.p. [°C]
				% N	% S		
<i>I</i>	Phenyl	C ₂₀ H ₁₂ N ₂ O ₃ S ₃	424.5	6.59 6.58	22.65 22.72	85.2	305-306
<i>II</i>	4-Bromophenyl	C ₂₀ H ₁₁ BrN ₂ O ₃ S ₃	503.4	5.56 5.56	19.10 19.16	88.2	255-258
<i>III</i>	4-Tolyl	C ₂₁ H ₁₄ N ₂ O ₃ S ₃	438.5	6.38 6.48	21.94 21.96	90.5	328-330
<i>IV</i>	4-Carboxyphenyl	C ₂₃ H ₁₆ N ₂ O ₆ S ₃	486.5	5.64 5.62	19.37 19.35	85.0	255-257
<i>V</i>	4-Methoxyphenyl	C ₂₁ H ₁₄ N ₂ O ₄ S ₃	454.5	6.16 6.37	21.16 20.90	82.0	263-265
<i>VI</i>	4-Chlorophenyl	C ₂₀ H ₁₁ ClN ₂ O ₃ S ₃	494.4	5.66 5.44	19.45 19.02	87.5	259-261
<i>VII</i>	4-Ethoxyphenyl	C ₂₂ H ₁₆ N ₂ O ₄ S ₃	486.6	5.97 6.27	20.52 20.80	85.2	260-262
<i>VIII</i>	Benzyl	C ₂₁ H ₁₄ N ₂ O ₃ S ₃	438.5	6.37 6.29	21.94 21.95	82.0	250-253
<i>IX</i>	Methyl	C ₁₅ H ₁₀ N ₂ O ₃ S ₃	362.4	7.72 7.77	26.54 26.49	85.0	210-212

Table 2
Spectral data of the synthesized compounds

Compound	λ_{\max} [nm]	$\log \epsilon$	λ_{\max} [nm]	$\log \epsilon$	λ_{\max} [nm]	$\log \epsilon$	$\tilde{\nu}(\text{C}=\text{O})$
<i>I</i>	249	4.06	329	4.23	438 460 i	4.70 4.63	1713
<i>II</i>	250	4.15	324	4.21	430 461 i	4.61 4.38	1712
<i>III</i>	249	4.05	328	4.20	438 460 i	4.70 4.63	1708
<i>IV</i>	250	4.00	325	4.15	435 460 i	4.68 4.60	1719
<i>V</i>	259	4.24	327	4.21	439 460 i	4.66 4.61	1705
<i>VI</i>	256	4.30	323	4.32	427 455 i	4.68 4.50	1712
<i>VII</i>	255	4.28	325	4.30	430 460 i	4.55 4.50	1709
<i>VIII</i>	244	4.00	328	4.20	438 440 i	4.70 4.61	1709
<i>IX</i>	240	4.08	322	4.23	424 461 i	4.60 4.19	1714

i = inflexion.

($\log \epsilon > 4$) in the last region in each case. The u.v. spectrum of 5-(4-nitrophenyl)-2-thiophenecarbaldehyde showed an absorption maximum at λ 311 nm ($\log \epsilon$ 4.16). Therefore the absorption maximum at ~ 325 nm on the spectra of the synthesized derivatives could belong to 5-(4-nitrophenyl)-2-thiophenecarbaldehyde residue while the band in the visible region (~ 435 nm) was a result of electron oscillations in the whole conjugated system of the molecule. Two conjugations could be assumed, *i.e.* either through the thione group of the rhodanine skeleton or through the carbonyl group bound in the cycle.

Experimental

Infrared spectra of the synthesized derivatives I–IX were recorded with a double-beam UR-10 Zeiss spectrophotometer in the region of 800–3600 cm^{-1} using KBr pellets (a sample size of 2 mg with 1 g potassium bromide).

Electronic absorption spectra were taken with a Specord UV VIS Zeiss spectrometer at 220–800 nm using cells of 10 mm thickness. The concentration of the measured compounds in dioxan solutions was $2-5 \times 10^{-5}$ M.

The starting 3-substituted rhodanines were prepared from the appropriate isothiocyanates and thioglycolic acid on a large scale [5] or by microsynthesis under the exactly defined conditions [6]. The used 5-(4-nitrophenyl)-2-thiophenecarbaldehyde was prepared by the modified Meerwein reaction of 2-thiophenecarbaldehyde with 4-nitrophenyldiazonium salt in the presence of copper(II) chloride as catalyst [7].

The 3-substituted rhodanines were condensed with 5-(4-nitrophenyl)-2-thiophenecarbaldehyde according to Brown's method [4].

The characterization of the prepared compounds is in Table 1 and their spectral data are assembled in Table 2.

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