

Isothiocyanates. XXXV.

3-Substituted rhodanines derived from (*p*-isothiocyanatophenyl)alkyl sulfides and sulfones

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The preparation of 13 new 3-substituted rhodanines derived from isothiocyanates containing sulfur beside that in the functional group is described in this work. Infrared and ultraviolet spectra of the synthesized derivatives are interpreted.

In connection with the preceding works [1, 2] dealing with nucleophilic addition of OH⁻ ions and amino groups, respectively, to isothiocyanates (ITC), it seemed useful to study also the reaction of ITC with thioglycolic acid [3].

So far, rhodanines on a large scale were prepared by reaction of the appropriate dithiocarbamate with monochloroacetic acid [4] and isothiocyanate with thioglycolic acid [5], respectively. However, thioglycolic acid is quantitatively added to isothiocyanates under exactly defined conditions. This fact was utilized in the microsynthesis of 3-substituted rhodanines. In this work, thioglycolic acid was added to (*p*-isothiocyanatophenyl)alkyl sulfides and sulfones.

Experimental

The appropriate (*p*-isothiocyanatophenyl)alkyl sulfides and (*p*-isothiocyanatophenyl)alkyl sulfones prepared from the corresponding amines by thiophosgene method [6] were used as starting products for the synthesis of rhodanines.

Infrared absorption spectra of the synthesized derivatives were obtained on a double-beam UR-20 (Zeiss, Jena) spectrophotometer in the 700–3600 cm⁻¹ range. The used concentration of compounds in chloroform was 0.025 M.

Ultraviolet absorption spectra were taken with a Specord UV VIS spectrometer at 200–350 nm using 10-mm cells. The concentration of the measured compounds in methanol was 5×10^{-5} M. The used methanol contained 1% of glacial acetic acid to prevent decomposition of rhodanines.

3-Substituted rhodanines

The isothiocyanate (1 mole) was dissolved in acetone (20 ml) under cooling and triethylamine buffer (20 ml) (1.6 ml of 2 N acetic acid and 0.96 ml of triethylamine filled with water up to 20 ml) containing thioglycolic acid (1.04 mmole) was added. The reaction mixture of pH 10 was placed into a water bath at 30°C for 1 hour. Then the solvent

Table 2

Infrared and ultraviolet spectra of the synthesized 3-substituted rhodanines

No.	$\lambda_{\max I}$ [nm]	$\log \epsilon$	$\lambda_{\max II}$ [nm]	$\log \epsilon$	$\bar{\nu}(C=O)$ [cm ⁻¹]	$\bar{\nu}_{as}(SO_2)$ [cm ⁻¹]	$\bar{\nu}_s(SO_2)$ [cm ⁻¹]
<i>I</i>	262	4.30	293	4.18	1746	—	—
<i>II</i>	263	4.29	294	4.23	1743	—	—
<i>III</i>	265	4.25	293	4.26	1754	—	—
<i>IV</i>	264	4.30	293	4.26	1755	—	—
<i>V</i>	264	4.27	293	4.22	1748	—	—
<i>VI</i>	264	4.26	293	4.20	1752	—	—
<i>VII</i>	257	4.11	297	4.10	1754	1317	1154
<i>VIII</i>	256	4.09	296	4.09	1753	1319	1142
<i>IX</i>	257	4.12	296	4.10	1765	1323	1146
<i>X</i>	257	4.08	297	4.08	1764	1322	1158
<i>XI</i>	257	4.13	297	4.12	1759	1326	1163
<i>XII</i>	264	4.27	294	4.22	1750	1325	1130 w
<i>XIII</i>	264	4.21	294	4.19	1746	1325 w	1133 vw

w — weak, vw — very weak.

It is evident from our observation that the lengthening of the alkyl chain does not make difficult the preparation of these compounds. All the prepared 3-substituted rhodanines after isolation from the reaction medium were yellow crystalline compounds.

Two absorption bands in the ultraviolet region at 256–265 and 293–297 nm, respectively (Table 2) were characteristic of the prepared 3-substituted rhodanines. The first absorption maximum (~ 260 nm) could be attributed to the so-called “N” conjugation (thioamide band) and the second one (~ 295 nm) to the “S” conjugation (dithiocarbamate band). Both bands were of high intensity ($\log \epsilon$ above 4). Introduction of the —S—R group (due to the free electron pair on the sulfur atom, a mesomeric “S” conjugation was possible) into the molecule of 3-phenylrhodanine caused a bathochromic shift of the first absorption band (with 3-phenylrhodanine λ_1 258 nm) while introduction of the —SO₂—R group (electron acceptor) manifested itself hypsochromically (except for derivatives *XII* and *XIII* with a long alkyl chain). The position of the second band practically did not change (Fig. 1).

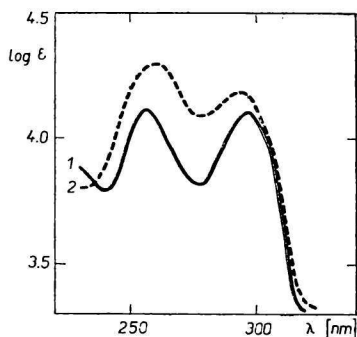


Fig. 1. Ultraviolet absorption spectra.

1. 3-(4-methylphenylthio)rhodanine;
2. 3-(4-methylphenylsulfonyl)rhodanine.

5×10^{-5} M solutions in methanol
(with 1% glacial acetic acid).

The characteristic wavenumbers of bonds of the prepared rhodanines are given in Table 2. With the increasing alkyl, bands belonging to stretching vibrations of C—H bonds were negligibly shifted to lower wavenumbers. The spectra of all investigated rhodanines showed very intensive absorption bands of stretching vibrations of C=O groups in the 1764—1743 cm^{-1} range. In case Z = SO₂, a shift to higher wavenumbers was observed (derivative I, when Z = S, showed a band at 1746 cm^{-1} while VII with Z = SO₂ at 1754 cm^{-1}) due to the electron-accepting properties of the functional SO₂ group. The bands belonging to vibrations of the C=C bonds of the aromatic system were observed at 1600—1500 cm^{-1} , the absorption band at 1500 cm^{-1} being much more intensive than that at 1600 cm^{-1} . The absorption bands belonging to deformation vibrations of C—H bonds of alkyl groups appeared in the range of 1478—1384 cm^{-1} being insignificant with some derivatives. With derivatives VII—XIII (Z = SO₂), intensive absorption bands $\bar{\nu}_{\text{as}}(\text{SO}_2)$ were observed in the region 1326—1317 cm^{-1} and a very intensive band $\bar{\nu}_s(\text{SO}_2)$ at 1163—1130 cm^{-1} . The position of these bands was not dependent on the character of the alkyl chain.

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